## THE SOIL SCIENCE SOCIETY OF FLORIDA

# PROCEEDINGS VOLUME X 1950

Tenth Annual Meeting of the Society
Winter Haven
June 21, 22 and 23, 1950

#### OFFICERS OF THE SOCIETY

#### 1951

RICHARD A. CARRIGAN	President
I. W. WANDER	Vice President
W. T. Forsee, Jr.	Member Executive Committee
R. V. ALLISON	Secretary-Treasurer
Retiring Officers listed on page 26	9.



#### ACKNOWLEDGMENTS

The Executive Committee, in behalf of the entire membership of the Society, wishes to express its sincere thanks to Commissioner Mayo and his Associates for the generous use of the Florida Citrus Building at Winter Haven and to Mr. Frank L. Holland, Manager, Florida Agricultural Institute, for his good help in so many ways in making local arrangements.

They also desire to express the good fortune they feel in having such distinguished workers from out of State present and take most valuable parts on the program as: Dr. I. J. Cunningham (New Zealand), Prof. A. L. Lang (Illinois); Drs. W. L. Nelson and Wreal L. Lott (North Carolina); Dr. Vincent Sauchelli (Maryland); Dr. Robert E. Lucas (Indiana); Dr. E. R. Purvis (New Jersey); Dr. James A. Naftel, (Alabama) and Major W. O. Robinson, Washington, D. C. (U.S.D.A.). They do have our very best thanks.

We feel no less gratitude, assuredly, to those workers in other countries who, though they could not be present at the meeting, went to great pains in preparing excellent manuscripts on the subject assigned in the effort at a broad review of trace element work in its relation to plant and animal health and growth on a world wide scale. These include Dr. Katherine Warington, Rothamsted Experimental Station (England); Dr. E. G. Mulder (Holland); Drs. H. G. Green and Ruth Alcroft, Veterinary Laboratory, Weymouth (England) and Mr. D. S. Riceman (Australia).

Finally, we are most particularly indebted to Dr. Edward M. Redding. Director of Research at the Charles F. Kettering Foundation, Dayton, Ohio for his splendid after dinner address. This gave us a most extraordinary insight into the vast role that chlorophyll plays in the development and maintenance of life on the earth in which it serves as an amazing link

of great power and vast mystery between the Sun and the Soil.

#### SUSTAINING MEMBERS

(1950)

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per Co., Calumet, Mich.

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Newport Industries, Inc., West Palm Beach, Fla.

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Serrales Everglades Farms, Inc., Miami, Fla.

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Weiss, M. M., Miami, Fla.

Weston, J. W., Ft. Lauderdale, Fla. White Belt Dairy, Miami, Fla.

Wilson & Toomer Fertilizer Company, Jacksonville, Fla.

Woods, F. J. and L. P., Tampa, Fla. Wray, Floyd L., Ft. Lauderdale, Fla.

Zipperer, J. O., Ft. Myers, Fla.

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#### NIGHT TRIP TO PHOSPHATE OPERATIONS

On the evening of June 21 a considerable number of members who had registered for the meetings went for a night tour of several of the local phosphate plants in the immediate neighborhood of Mulberry.

This trip was arranged for by Mr. Frank Holland, Manager, Florida Agricultural Research Institute and Mr. Vincent Souchelli, Director of Research, Davidson Chemical Company of Baltimore and Mulberry.

The cordial cooperation of the management of the several mills was greatly appreciated and exceedingly helpful in giving those on the tour a really good view of the colossal scale upon which these phosphate operations are conducted in Florida.

#### DEDICATION OF PROCEEDINGS VOLUME X

In the course of developing the program covered by Volume X an earnest effort was made to bring together in summary form the outstanding results that have been accomplished during the past quarter century through the use of certain of the so-called trace or minor elements in the improvement of health and growth in both plants and animals. The important relationship of human health to these factors was not included in this program as it was in the first symposium in 1940 (Proc. Vol. II) since this would have made it much too ponderous for the time allotted. Perhaps this can be the subject of a further and separate review in the near future.

In any event the Executive Committee of the Society is pleased with the results of its efforts and proud of the many excellent contributions from all parts of the United States and many parts of the world that are included in this report. The members of the Committee are no less proud of this opportunity to dedicate this volume to the fine group of workers who have so graciously accepted Honorary Life Membership in the Society on the occasion of this, its Tenth Annual Meeting. Each and every one of these men have made notable contributions to soil or plant science or to some phase of animal health as related thereto. No welcome could be more hearty or sincere than that which we now extend to them as full-fledged members of our group.

Dr. Selman A. Waksman, New Brunswick, N. J.

Dr. Charles F. Kettering, Dayton, O. Sir John Russell, Campsfield Wood, England

Dr. M. F. Miller, Columbia, Mo.

Dr. F. J. Alway, St. Paul, Minn.

Dr. S. N. Winogradsky, Pasteur Institute, France

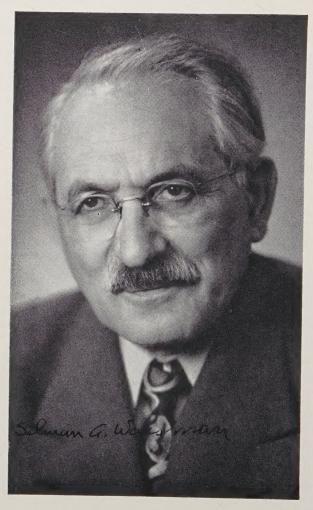
Dr. Oswald Schreiner, Chevy Chase,

Dr. W. P. Kelley, Berkley, Calif.

Dr. D. J. Hissink, Bussum, Holland

Dr. Charles E. Millar, East Lansing, Michigan

Dr. John G. DuPuis, M.D., Our Country Doctor, Miami, Florida



SELMAN A. WAKSMAN

#### SELMAN A. WAKSMAN

Dr. Waksman was born July 2, 1888, in Priluka, a small town in the Ukraine, Russia. His parents were Jacob and Fradia (London) Waksman. He received his early education from private tutors. After graduating in 1910 from the Fifth Gymnasium in Odessa, he left for the United States. He entered the College of Agriculture of Rutgers University in 1911

and received his bachelor of science in 1915. He became a naturalized citizen the same year. He then was appointed research assistant in soil microbiology under Dr. J. G. Lipman at the New Jersey Agricultural Experiment Station, and later Research Fellow at the University of California. He obtained a master of science degree from Rutgers University in 1916 and a doctor of philosophy degree from the University of California in 1918, majoring under Prof. H. Brailsford Robertson in Biochemistry.

He received an appointment the same year as microbiologist at the New Jersey Agricultural Experiment Station at New Brunswick, New Jersey, and lecturer in soil microbiology at Rutgers University. He became associate professor in 1925, and in 1930 was made professor. He now heads the Microbiology Department, College of Agriculture and Experiment Station, Rutgers University and has recently been made Director of the New Institute of Microbiology.

In 1931, he was invited to organize a division of marine bacteriology at the newly established Woods Hole Oceanographic Institution and was appointed marine bacteriologist of that institution, of which he was later made a trustee.

He is a member, honorary member, or fellow of a number of scientific societies in this country and abroad (Germany, India, Russia, Sweden, Mexico, France, Brazil, Spain). Among the American Societies to which he belongs are the Society of American Bacteriologists, of which he is a former president, the National Academy of Sciences, and the Soil Science Society of Florida of which he is a Charter member. He won the Nitrate of Soda Nitrogen Research Award in 1929, was president of Commission III on Soil Microbiology of the International Society of Soil Science (1927-1935), and was elected as corresponding member of the French Academy of Sciences in 1937. He is also a member of Phi Beta Kappa and of Sigma Xi being President of the Rutgers Chapter of the latter organization.

In the summers of 1946 and 1947, Dr. Waksman lectured before scientific groups in Europe and was given an honorary degree of doctor of medicine by the University of Liege in Belgium. He holds also honorary degrees of doctor of science, awarded to him by Rutgers in 1942, by Princeton University in 1947, and University of Madrid in 1950; also an honorary degree of doctor of laws from Yeshiva University, New York, in 1948.

Dr. Waksman's work in his field has been recognized by numerous scientific and other societies in recent years. He received the Passano Foundation Award in 1947; the Emil Christian Hansen medal and award from the Carlsberg Laboratories in Denmark the same year; the New Jersey Agricultural Society medal; the Albert and Mary Lasker Award by the American Public Health Association, and the Amory Award by the American Academy of Arts & Sciences, all in 1948, and many others.

He has published more than 300 scientific papers, and has written, alone or with others, eight books. Among these are "Enzymes," 1926; "Principles of Soil Microbiology," 1927, 1932; "The Soil and the Microbe," 1932; "Humus," 1936, 1938; "Microbial Antagonisms and Antibiotic Substances," 1945, 1947, and "The Literature on Streptomycin, 1944-1948," 1948; "Actinomycetes," 1950. Another work, edited by Dr. Waksman, is "Streptomycin—Nature and Practical Applications."



CHARLES FRANKLIN KETTERING

#### CHARLES FRANKLIN KETTERING

Charles Franklin Kettering, Vice-President and Research Consultant of General Motors Corporation, was born on a farm near Loudonville, Ohio, August 29, 1876. He was educated in the county district school, Wooster College, and Ohio State University, graduating in 1904 with the degree EE in ME. He was elected to the honorary fraternities Sigma Xi and Tau Beta Pi.

Following his collegiate work, Dr. Kettering became designer and in-

ventor for the National Cash Register Company, remaining with that organization for five years. He was inventor of the electric cash register, the telephonic credit system, and numerous improvements in accounting and calculating machinery.

In 1909, he became associated with Edward A. Deeds in the organization of the Dayton Engineering Laboratories Company (Delco) for the purpose of developing electrical starting, lighting, and ignition apparatus which he had invented. His invention of the Delco-Light farm electrification system was also completed during this period.

In 1916, he established a private research laboratory which was taken over in 1920 by General Motors and in 1925 moved to Detroit as the Research Laboratories Division of General Motors Corporation. The latter organization, operating under Dr. Kettering's supervision, has been responsible for a large number of important contributions to automotive transportation, including Ethyl gasoline, Duco lacquer, crankcase ventilation, and others.

Another of Dr. Kettering's developments was the two-cycle Diesel engine which has found wide application in the railway and industrial fields. His most recent work has been concerned with high-compression engines for automobiles. In June, 1947, he announced the development of a gasoline engine of 12.5 to 1 compression ratio, giving 35 to 40 per cent better fuel economy than conventional engines. He is the recipient of 174 patents on automotive and related inventions.

Dr. Kettering's widespread interests have led him into many other technical fields. He is the inventor of a fever machine which has proved effective in the treatment of several heretofore incurable diseases.

For most of his life. Dr. Kettering has been actively interested in photosynthesis and the problems related to improvement of soils and agriculture in general. In 1929, he established the Charles F. Kettering Foundation which has carried on research in photosynthesis, cancer, and venereal disease treatment. He has actively supported Soil Conservation and Soil Research, particularly in the field of the use of trace elements.

In addition to his association with General Motors, Dr. Kettering is a Director of the National Cash Register Company, the Flexible Company, and the Mead Corporation. He is Chairman of the Winters National Bank & Trust Company. During World War II, he was Chairman of the National Inventors Council and the National Patent Planning Commission. He is a Trustee of Ohio State University.

Noteworthy among the honors that have come to him are the Sullivant Medal, the John Scott Memorial Award, the Franklin Gold Medal, the Gold Key of the American Congress of Physical Therapy, the Honor Medal Award of the A.S.M.E., and the John Fritz Medal Award. He is the recipient of honorary degrees from 21 different universities and is an honorary fellow of the National Academy of Sciences. He is Past-President of the American Association for the Advancement of Science and the Society of Automotive Engineers.

While Dr. Kettering's accomplishments in various fields of science and research have won him many honors and degrees, he esteems most highly the tag which his fellow workers hung on him years ago and which has clung to him ever since-"Boss Ket."



EDWARD JOHN RUSSELL

#### EDWARD JOHN RUSSELL

(England)

Sir John Russell was born in 1872. He was trained at the Universities of Wales and Manchester, where his chief interest was in Chemistry. His first scientific appointment, in 1897, was as lecturer in Chemistry at Manchester. In 1901 he moved to the Agricultural College, Wye, as head of the Chemical Department. In 1907 he was appointed Soil Chemist at Rothamsted Experimental Station, and five years later, on the resignation of Sir Daniel Hall, he became Director, a post which he held until his retirement in 1943, soon after the Station celebrated its centenary.

His research work has been mainly concerned with soil fertility, at first on the microbiological aspects of the subject and later on the effect of fertilizers on yield, composition and quality of crops.

Of his many publications, the most widely known is his textbook "Soil Conditions and Plant Growth," which has passed through seven editions and has been translated into many languages.

He was elected a Fellow of the Royal Society in 1917, and is an honorary member of many foreign learned societies. In recognition of his services in the food production campaign during the 1914-18 war he received the Order of the British Empire in 1918, and was knighted in 1922. He has been President of the International Society of Soil Science, and in 1949 was President of the British Association for the Advancement of Science, the first agricultural scientist to be so honoured.

Sir John has travelled widely, especially in the countries of the British Empire, and has an extensive first-hand knowledge of the problems of crop production in many parts of the world. Since his retirement, he has continued his writing and traveling, though this was interrupted by a serious illness in 1944 from which he has happily made a remarkable recovery. His present interest is mainly in the problem of providing an adequate world food supply. As his Presidential Address to the British Association shows, he takes an optimistic view of this, and is confident that scientific research, if properly applied, can find a solution.



MERRITT FINLEY MILLER

#### MERRITT FINLEY MILLER

Dr. Miller was born in Grove City, Ohio, on July 7, 1875 where he was reared on a farm. His parents were E. Ed and Elizabeth (Demorest) Miller. He received his early education in a typical one-room country school of that time, and later did preparatory work at Ohio Wesleyan University.

In 1900 Dr. Miller completed his B.S.A. degree at Ohio State University, and in 1901 took his M.S.A. degree at Cornell. He studied abroad in Europe at two different times, 1910-1911 at the University of Gottingen, and 1933-1934 at the University of Munich. He received the honorary degree of Doctor of Agriculture from Kansas State College in 1938.

During 1901-1902 Dr. Miller served as Assistant in the Federal Soil Survey, and in December 1902 he married Alice G. Thompson. Many years later, December 1914, he married Grace Ernst. To these unions were born three sons and one daughter, Edward Ernst, Elizabeth Marie, Robert Demorest and Daniel Weber.

Dr. Miller served as Instructor in Agronomy at Ohio State University in 1902-1903, and as Professor of Agronomy at the University of Missouri from 1904 to 1914. From 1914 to 1938 he was Professor of Soils and Chairman of the Department of Soils, and simultaneously served as Assistant Dean of the College of Agriculture from 1929 to 1938. In 1938 he was made Dean of the College of Agriculture at the University of Missouri, in which position he served in a most distinguished manner until his retirement in 1945. He then became Dean Emeritus of the College, Director Emeritus of the Experiment Station and Professor Emeritus of Soils, in which capacities he has continued his interest in the work of the Institution in a most active way. This has expressed itself in a most permanent and beneficial way by the frequent scientific papers and bulletins which he has published and is publishing during this period.

Dean Miller's principal interests have been in the field of soil fertility and erosion; field classification of soils, and factors affecting the nitrogen and carbon levels in soils. His contributions in his chosen field have been numerous and important, perhaps none moreso, however, than those to the state and national program of soil conservation that has made so much progress during the past quarter century.

Professor Miller is a member of many active and honorary societies and organizations, including: Alpha Zeta; Gamma Sigma Delta; Sigma Xi; American Society of Agronomy (President 1923); Soil Science Society of America; International Society of Soil Science; and the American Association for the Advancement of Science (Chairman, Section O).



FREDERICK J. ALWAY

#### FREDERICK JAMES ALWAY

Dr. Alway was born May 28, 1874 in Waterford, Ontario, and received his early training in Canadian schools. In 1894 he received his B.A. degree from the University of Toronto, and in 1897 his Ph.D. degree from the University of Heidelberg.

From 1898 to 1906 Dr. Alway was professor of Chemistry at Nebraska Wesleyan University, during which period he was particularly interested in research on the reduction of nitro compounds; hydroxylamino—and nitroso compounds and in the soils of the Northern Steppes. From 1906 to 1913 he was Professor of Agricultural Chemistry at the University of Nebraska, during which period his research interests were largely in the bleaching of flour; prairie soils; soil humus; soil moisture; and dry farming.

From 1913 to 1942 Dr. Alway was Professor of Soil Chemistry and Chief of the Division of Soils in the Agricultural Experiment Station at the University of Minnesota. During this period his research interest was largely in glacial, peat and sandy soils; phosphates; the soil requirements of alfalfa; forest soil characteristics and the contributions of sulfur to the soil from the air. In this latter work, Dr. Alway did much in recreating scientific interest in sulfur as an essential element in plant growth when he referred to it in one of his national lectures as "the forgotten element" and, thus, gave much impetus to its further study.

Dr. Alway was a member of the Fertilizer Sub-Committee of the National Research Council; the A.A.F.; the American Chemical Society; American Soil Survey Association (President 1923); American Association for the Advancement of Science; American Society of Agronomy (President 1940); Swêdish Peat Society.

At the time of his retirement from active duty in 1942 Dr. Alway was appointed Professor Emeritus of Soil Chemistry and has continued his residence in St. Paul at 1386 Grantham Street since that time.



#### SERGEI NIKOLAEVITCH WINOGRADSKY

(France)

Dr. Winogradsky was born on September 1, 1856, in the city of Kiev, heart of the Ukraine region, Russia.

It will not be possible, of course, to review in detail Dr. Winogradsky's training, his difficult experiences due to his several moves to foreign countries on three different occasions (Germany, Switzerland, France) due to war, or for other disturbing reasons, and his remarkable life achievements even under these difficult conditions. His mature life, however, according to a remarkably complete and carefully written biographical sketch pre-

pared by Dr. S. A. Waksman on the occasion of Dr. Winogradsky's ninetieth birthday, and published in Soil Science Volume 62, pp. 197-226, 1946, might well be divided into 7 important periods, as follows:

- 1. The first St. Petersburg period (1881-1884), when his interest in science matured. Though this may be considered as still a period of intensive training, Winogradsky began and completed his first scientific problem, which proved to be highly successful (work with wine yeast, Mycoderma vini Desm). During this period, he worked in the laboratory of plant physiology of the university.
- 2. The Strassburg period (1885-1888). Here he carried out his first investigations on the autotrophic bacteria. The problems dealing with the sulfur and iron bacteria were begun and completed at the botanical laboratory of the university under deBary.
- 3. The Zurich period (1888-1891). The study of the organisms concerned in the process of nitrification was begun and nearly completed at the agricultural faculty of the polytechnicum and at the hygienic laboratory of the university.
- 4. The second St. Petersburg period (1891-1905). This began with research activities and ended in administration work, the latter being largely responsible for his subsequent temporary retirement from both. The most important research problems dating to this period concerned the fixation of atmospheric nitrogen and the retting of flax. This work was done at the Institute of Experimental Medicine.
- 5. The period of transition and rest (1905-1922). These 17 years were spent by Winogradsky on his estates in the Ukraine, away from scientific work. As a result of political upheaval following the World War and the revolution, he was eventually forced to leave his native country forever. After a few months spent in Jugoslavia, he finally arrived at the Pasteur Institute in France.
- 6. The active Brie-Comte-Robert period (1922-1940), which signalized a return to scientific work. The problems considered were largely connected with the broad aspects of soil microbiology. This work was done in the Division of Agricultural Microbiology of the Pasteur Institute.
- 7. The period of forced retirement (1940-.....), following the invasion of France.

The name of Winogradsky has assumed a permanent place in bacteriology through the profound influence of his investigations upon the subsequent development of many important branches of the science. As a result of the brilliant and epoch-making investigations of Louis Pasteur, Ferdinand Cohn, and Robert Koch, bacteriology developed rapidly from a mere biological curiosity into a science of great practical importance, with numerous ramifications, stretching into the domains of medicine, agriculture, industry and certain arts.

Dr. Winogradsky is still living at Brie-Comte-Robert near Paris at the age of 94. Under date of 1949 there appeared a large book entitled "Microbiology of the Soil" (MICROBIOLOGIE DU SOL) containing 861 pages which gives a very good idea of the remarkable life he has lived, filled with accomplishments, many of them developed under very great difficulties but, above all, a life that has been replete with devotion to his

science.



WALTER PEARSON KELLEY

#### WALTER PEARSON KELLEY

Dr. Kelley was born February 19, 1878 in Franklin, Kentucky. He received his B.S. degree from the University of Kentucky in 1904; his M.S. from Purdue University in 1907; and his Ph.D. in 1912 from the University of California, which University, in June of 1950, also awarded him the honorary degree of LLD.

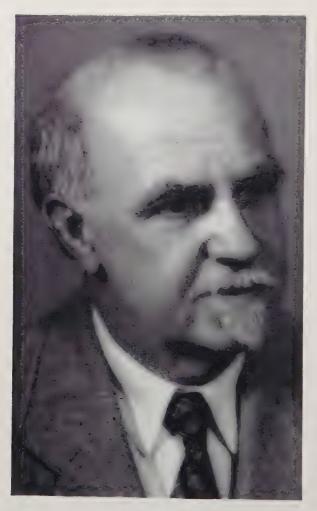
From 1905 to 1908 Dr. Kelley was Assistant Chemist at the Purdue Experiment Station, and Chemist at the Hawaiian Experiment Station from 1908 to 1914. He then became Agricultural Chemist at the Citrus Experiment Station, Riverside, California. In 1939 he went to Berkeley as Soil Chemist and Head of the Division of Soils in the University, in which position he continued until his retirement in 1948.

Dr. Kelley's principal interest in research has centered around nitrogen utilization by rice; effect of heat on soils; composition of Hawaiian soils; forms of nitrogen in soils; nitrification; effect of boron on citrus and walnut trees; cation exchange; alkali soils; crystallinity of soil colloids; crystal structure in relation to base exchange; clay minerals of soils; and the interrelationships of soil science and geology.

According to one of his close associates, "Dr. Kelley's contribution to our fundamental knowledge of soil chemistry has been extremely important. In 1931, with W. H. Dore and S. M. Brown, he was able to show from X-ray diffraction studies that soil colloids are crystalline and not amorphous as was thought until that time. This discovery gave great impetus to the study of clay chemistry and as a result of this many of the soil minerals have been separated out and their chemistry studied. Much of this latter work has been carried out by Dr. Kelley and is described in a long series of papers in the journals of soil science and mineralogy. The work is also reported by him in an American Chemical Society Monograph on Base Exchange."

Dr. Kelley also has achieved an international reputation for his work on alkali soils. This work was begun in 1920 and has been reported in some twenty odd papers, and also in a monograph on alkali soils, which he has just completed. In these researches, reclamation methods were developed which are now being employed throughout the world in connection with this serious problem of irrigated agriculture.

Among his many affiliations with scientific and other organizations are included American Association for the Advancement of Science; American Chemical Society; Fellow of American Society of Agronomy (President 1930); Soil Science Society of America; International Society of Soil Science; Geophysical Union and Western Society of Soil Science.



OSWALD SCHREINER

Dr. Schreiner was Chief of Soil Fertility Investigations in the U.S. Department of Agriculture for more than 40 years. He is now retired but still connected with the department as collaborator.

The research work on the fundamental principles of soil fertility, especially those relating to the chemistry and biochemistry of soil organic matter or humus and to its functions in promoting or hindering plant development, won for Dr. Schreiner a prominent place of leadership among soil scientists and agronomists at home and abroad. To the laboratory under his direction belongs the credit for the chemical discovery, physical separation and plant physiological study of over fifty new soil compounds, which has materially altered the fundamental conception of

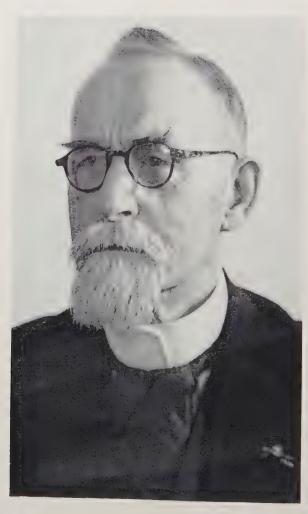
soil humus and its formation and transformation by plants and microorganisms and its effects and functions in crop production. He is the inventor of the Schreiner colorimeter and designer of colorimetric methods, which, on account of their great applicability to various lines of soil and plant research have been widely used for the determination of small quantities of plant nutrients in chemical laboratories in this country and abroad, as was also his triangle system for studying and determining fertilizer requirements of soils and crops under field conditions.

He made a special study of soil fertility and its maintenance, causes of unproductive soils, transformation of humus by biochemical factors, origin of organic constituents in soils and means for the improvement of unproductive soils by fertilizers, manures, crop rotations and the use of special chemicals including some of the minor elements. This field work included the establishment of more than twenty field stations along the Atlantic seaboard from Maine to Florida and in a number of western states, with fertilizer tests made with potatoes, cotton, celery, lettuce, sorghum, sugar beets, sugar cane, corn, clover, pecans, citrus fruits and many other crops.

Dr. Schreiner won a national reputation by his many lectures at agricultural colleges and before farmers' institutes and clubs and scientific societies. Many honors have been awarded him for his chemical and agricultural researches, three medals for proficiency in chemistry and other sciences while attending the University of Maryland, and while attending the University of Wisconsin he was elected to the honorary society of Phi Beta Kappa and Sigma Xi and was awarded the Ebert prize for his researches on the chemistry of the volatile oil hydrocarbons. The Franklin Institute awarded him its Longstoreth medal of merit "for important researches in agricultural chemistry."

As Chairman of the Organizing Committee he contributed greatly to the success of the International Soil Science Congress in Washington in 1929. He was elected Fellow in the American Association for the Advancement of Science and the American Society of Agronomy and is a member of the American Chemical Society, the American Society of Biological Chemists, Washington Academy of Sciences, Botanical Society of America, International Society of Soil Science, International Society of Sugar Cane Technologists, the Cosmos Club, and the Association of Official Agricultural Chemists of which he is a past president and many other societies.

Dr. Schreiner's work on soils and fertilizers has received national and international recognition. In this connection he has traveled extensively throughout the United States and many foreign countries, including England, Scotland and Wales, Germany, France, Holland and Belgium, Japan, China, Philippines, Malay States, Sumatra, Java, Bali, as well as Cuba, Puerto Rica and Hawaii. He investigated the potash hunger diseases of potatoes and cotton and first described the characteristic foliage symptoms and reactions during the first World War, which work later developed into that long series of soil and fertilizer studies known as the "hunger symptoms of crops" and led to the many plant and soil test methods for the determination of plant nutrient deficiencies and fertilizer requirements of crops.



DAVID JACOBUS HISSINK

#### DAVID JACOBUS HISSINK

#### (Holland)

Dr. Hissink was born October 22, 1874 in Kampen, Holland. He was trained in the local schools and in the "Gymnasium" until 1893 when he entered the University of Amsterdam, where he continued his studies until 1899, when he received his doctor's degree. The years 1900 to 1903 were spent in the Dutch East Indies.

In March of 1903, Dr. Hissink went to the Agricultural Experiment Station at Goes, and in 1904 became the Director of that Station in which capacity he continued until 1907. From April of 1907 to May of 1916 he served as Director of the Agricultural Experiment Station at Wageningen. From May of 1916 to May of 1926 he served as Director of the Soil Science Division of the Agricultural Experiment Station in Groningen, and in May of 1926 he became Director of the Soil Science Institute in that same city, in which capacity he served until his retirement in 1939 at the age of 65.

Although an extremely energetic and effective worker in the International Society of Soil Science and many other public service organizations, Dr. Hissink found time for a very considerable amount of writing, in addition to the extensive administrative duties to which his position obligated him all the way along. His list of publications in Dutch and other journals is very impressive, numbering nearly 350 on a wide variety of subjects largely relating to soil science.

Doubtless the work for which Dr. Hissink is best known, and for which he will be long remembered in a personal as well as professional way, is his development and application of the principal of base exchange. His most important application of this principal was in the removal of the salt from the heavy clay soils formerly occupied by the sea in the extensive reclamation areas for which Holland is famous. What Dr. Hissink did, in its simplest terms, was to convert the highly plastic, impervious sodium clays, practically unleachable in their natural state, to comparatively pervious, leachable calcium clays through the use of gypsum.

"Basenaustausch" is the term in German and Dutch literature for which Dr. Hissing is probably more responsible than any other one man, at least insofar as it relates to soil science and finds both practical and scientific applications, therein.

Dr. Hissink is a member of many National and International societies and has received many honors from foreign governments and more than once from the Dutch Government, the last being a Knighthood bestowed at the time of his retirement in 1939. He continues in a quiet life at s'Jacoblaan 37, Bussum, Holland, whence he keeps a keen contact with the societies and journals he has helped to build, and still is an active adviser in the research work on the soils of the Zuiderzee.



CHARLES ERNEST MILLAR

#### CHARLES ERNEST MILLAR

Dr. Millar was born on a farm in Coles County, Illinois, June 23, 1885. He attended high school in Mattoon, Illinois, and received his B.S. and M.S. (in chemistry) from the University of Illinois in 1909 and 1911 respectively. Later he received his B.S. in Agriculture from Kansas State College in 1915, and his Ph.D. from the University of Wisconsin in 1923.

He was Assistant in Chemistry at Kansas State College from 1910-1913; Assistant in Agronomy, 1913-1914, and Instructor in Agronomy, 1914-1915; Assistant Professor in Soils at Michigan State College, 1915-1918; Associate Professor, 1918-1925; and Professor, 1925-1930. Dr. Millar became Head of the Department of Soils at Michigan State College in 1930 and continued in this position until his retirement in 1950, since which time he has been Professor Emeritus of Soils.

Dr. Millar is a member of Phi Lambda Upsilon, Alpha Zeta, Phi Kappa Phi, Phi Sigma and Sigma Xi. He was also awarded the Diploma of Merit by the State Board of Agriculture, governing body of Michigan State College, in appreciation of his long and effective service to Michigan agriculture. He is also a Fellow of the American Society for the Advancement of Science (Secretary of Section O—Agriculture) and Fellow of the American Society of Agronomy (Chairman Soils Section, 1935).

As his principal fields of interest, Dr. Millar was always found spending most of his spare time with his students and in the pursuit of special problems in his chosen field of soil fertility, especially as it relates to crop production. During his teaching career time was found by Millar for two books—Soils and Soil Management, by Webb Publishing Company, and Fundamentals of Soil Science (with Dr. Turk) by John Wiley and Sons.



JOHN GORDON DUPUIS, M.D.

#### JOHN GORDON DUPUIS, M.D.

(Our Country Doctor)

Dr. DuPuis was born in Alachua County, Florida, September 25, 1875. His parents were John Samuel and Mary Lohman DuPuis. In January 1899 he married Katherine Elizabeth Beyer in Paducah, Kentucky. To this union one son was born, John G. DuPuis, Jr.

Dr. DuPuis received his M.D. degree from the University of Louisville in June 1898, only shortly previous to his coming to Florida. He also has studied in the New York Post Graduate Medical School.

For more than 50 years Dr. DuPuis has served Miami and Dade County as a Country Doctor, in all the hallowed spirit and traditions of service that the term implies. It is because of this long, faithful and courageous service that the Society has requested his permission to include him as OUR Country Doctor among those whom we have elected to honorary life membership on the occasion of the Tenth Annual Meeting.

It would be very difficult for most people to imagine what Dr. DuPuis saw when he got off the train on October 28, 1898 at Lemon City, at that time scarcely an outpost of the Village of Miami which was still 5 miles farther south; or to realize that the small shack in which he started his practice of medicine shortly following his arrival stood very near the busy corner (6045 N.E. Second Avenue) on which his office now stands.

Along with the weary hours and busy routine of his medical work, Dr. DuPuis always found time, somehow, for a great many other public service activities of the type that always prove themselves indispensable elements in the development of a young pioneer community of the type in which he found himself, and of which he proceeded to make himself a truly integral part. In the first place, he gave much time to the development of church facilities in this new area and, through the years, took an active and frequently an aggressive part in a wide variety of civic organizations for the highly important part they always play in community progress. These included work on/or with church boards; school boards; drainage boards; Chamber of Commerce; State and County Medical Associations; Farm Bureau; Dairy Association; President, Dutch Belted Cattle Association of America; and many other associations.

Likewise, Dr. DuPuis very early decided that one of the most outstanding needs for children in this pioneer community was a better and more abundant milk supply. From this very humble beginning, which first started with his own family cow, there gradually emerged the great White Belt Dairy now employing hundreds of people, and which is still serving the Miami area as one of the largest and most modern individually owned dairies in the Southeast.

Thus, Dr. DuPuis has served this Florida community not only through its first, and only, outbreak of yellow fever and seventeen hurricanes, but all of the people all of the time, regardless of race, religion or financial circumstances, through more than half a century. He is now the only charter member of the Dade County Medical Association who is still active.

His great love of plants doubtless brings Dr. DuPuis closer to the soil than anything else. In his intense hobby for gardening, he accomplishes most remarkable things in the short time he is able to find for this work each day, especially in the field of tropical plants. His decided interest in plant health thus gives him a quick appreciation of the direct relationship of plant composition and health to the fertility level of the soil on the one hand and, on the other, to health and well being of animals, as well as men, who must live on them. Thus, through the channels of his medical wisdom, fortified by such an understanding, the relationship of soil to health has been brought by him to the attention of many people, not only in behalf of their well being and that of their immediate families, but for the health and well being of animals as well.

#### Institut Pasteur

BRIE-COMTE-ROBERT

(SEINE-&-MARNE)

Brie-Comte-Robert, July 29-th, 1950

Dr. R. V. ALLISON, Secretary-Treasurer, The Soil Science Society of Florida, BELLE GLADE, Florida, U. S. AMERICA.

Dear Dr. Allison,

Your letter of June 28-th I have duly received, and I am very touched by the honour the Soil Society of Florida has done me in electing me to an honourary life membership.

The photographe you ask for, I am mailing you, under separate cover,

by ordinary mail.

Meanwhile, the copy of Vol. VIII of the Proceedings has also reached me, for which I thank you very much.

With my kindest regards and best wishes,

I remain,

Yours sincerely,

S. Winogradsky.

Department of Microbiology Agricultural Experiment Station New Brunswick, N. J.

... We have just returned (from Europe) and I hasten to ... tell you how highly honored I feel to have been elected to Honorary Life Membership in the Soil Science Society of Florida.

(Signed) Selman A. Waksman, Microbiologist

Charles F. Kettering Foundation Dayton, Ohio

Thanks for your kind letter of June 28th. I appreciate being included among the notables.

(Signed) Ket C. F. Kettering

Campsfield Wood Woodstock, Oxon., England

Your letter . . . informing me that the Soil Science Society of Florida had elected me to Honorary Life Membership gave me very great pleasure, and I am indeed proud of the honor they have conferred upon me.

(Signed) E. J. Russell

514 High Street Columbia, Mo.

I truly appreciate the honor the Society is bestowing on me although I do not feel that it is deserved.

(Signed) M. F. Miller

1386 Grantham Street St. Paul, Minn.

I greatly appreciate the honor of the action taken by the Executive Committee in electing me to Honorary Life Membership in the Society.

(Signed) F. J. Alway

College of Agriculture Division of Soils Berkley, California

I am of course happy to accept Honorary Life Membership in the Soil Science Society of Florida. Indeed I am grateful for this honor.

(Signed) W. P. Kelley

21 Primrose Drive Chevy Chase 15, Md.

I feel greatly honored by  $\ldots$  my election to Honorary Life Membership in the Soil Science Society of Florida.

(Signed) Oswald Schreiner

Burgemeester's Jacobeaan 37 Bussum, Holland

The Soil Science Society may be sure that I feel it is a great honor that my name was included in the group of Soil Scientists elected to Honorary Life Membership...and it is a great pleasure for me to accept this honor.

(Signed) D. J. Hissink

Department of Soil Science Michigan State College East Lansing, Mich.

This action is indeed an honor, and I greatly appreciate being included among the first ten men to receive this distinction from your Society.

(Signed) C. E. Millar

6043 N. E. 2nd Avenue Miami 38, Florida

I wish to express my appreciation to the Executive Committee of the Society. I consider it a great honor to be included in the group which the Society has elected to Honorary Life Membership at its tenth annual meeting.

(Signed) J. G. DuPuis, M.D.



EDWARD MACARTHUR REDDING

#### EDWARD MACARTHUR REDDING

Dr. Redding was born October 27, 1915. He received his B.S. degree in Chemical Engineering at the University of Denver in 1938 and his Sc.D. degree in the same field from Massachusetts Institute of Technology in 1942. During 1941-2 he was engaged in Classified Research (NRDC) at M.I.T. From 1942 to the present time Dr. Redding's activities and accomplishments are listed briefly through the periods in which they fall:

1942-1945 U. S. Navy, Bureau of Aeronautics, Power Plant Design Branch, as a Naval Officer (Lt. Comdr. USNR), was active in coordinating development of turbo-jet and ram-jet engines for the Navy and research on related problems of high temperature alloys and combustion. Received commendation for work from the Secretary of the Navy.

Member, National Advisory Committee for Aeronautics Subcommittee for Combustion and Heat Resisting Alloys; Co-author of report by Jet Propelled Missiles Panel, Coordinator of Research and Development U.S. Navy.

1946-1948 North American Aviation, Inc. Aerophysics Laboratory

Co-originator and Assistant Technical Director of the Aerophysics Laboratory, organized to carry out research and development on guided missiles.

Member, National Advisory Committee for Aeronautics Subcommittee for Combustion. Specialized on rocket motor research and development.

1948 Massachusetts Institute of Technology, Research Staff

Participated in an evaluation study and co-author of a report for the Atomic Energy Commission on certain phases of its nuclear power program.

1948 to present Charles F. Kettering Foundation, Director of Research

In charge of coordinating and guiding the research program which is principally in the field of photosynthesis. With the exception of some preliminary laboratory work at the Dayton headquarters, most of the research is carried out by other agencies under contract. These agencies are mostly universities. A small part of the program is devoted to medical research.

Member American Chemical Society, American Institute of Chemical Engineers, Ohio Academy of Science, American Association for the Advancement of Science, Sigma Xi, Phycological Society, Soil Science Society of Florida.

### PHOTOSYNTHESIS—A LINK BETWEEN THE SUN AND THE SOIL

#### EDWARD M. REDDING\*

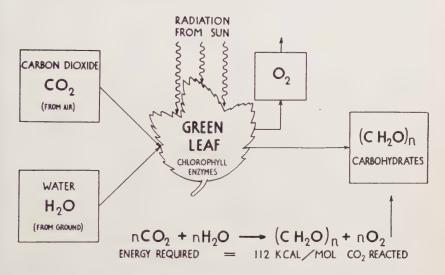
Practically every research worker who talks on the subject of photosynthesis presents a different point of view—his own. There are these many points of view because of the complexity of the problem, the differences in opinion, and the relative lack of success to date in solving the problem. The approach to the problem recently taken by the Charles F. Kettering Foundation is rather unique, but it is believed that tangible results will be forthcoming within a relatively short period.

Mr. Charles F. Kettering established the Foundation in 1929 for the purpose of financing research on photosynthesis and other problems, the solution to which would benefit mankind in general. A photosynthesis research project was started at Antioch College in Yellow Springs, Ohio, under the direction of Dr. O. L. Inman in 1930. This project has continued until the present time and is still operating at about the original level of activity. Until fairly recently, it was the only major project financed by the Foundation. Then, just before World War II, the Fever Therapy machine was developed for the treatment of venereal disease by the Foundation at the Miami Valley Hospital, Dayton, Ohio.

The photosynthesis research group at Antioch College concentrated on the study of chlorophyll, the green pigment in all photosynthesizing plants and which is generally credited with being the agent which absorbs the light energy used in the photosynthesis process. About two years ago, the decision was made to initiate more projects at other institutions and to attack the problem in a somewhat more basic fashion. This line of attack will be explained later.

Perhaps it would be helpful to discuss the more elementary phases of the photosynthesis process at this point. Figure 1 is a simplified picture of the primary photosynthesis reaction. Water and carbon dioxide combine with the addition of energy obtained from sunlight to form carbohydrates and release oxygen gas. This reaction has never been accomplished outside the green leaves of plants. These leaves contain chlorophyll and several other pigments, enzymes (biological catalysts of high molecular weight), inorganic and organic salts, and other materials of unknown function. This simple reaction as shown does not touch upon the important subject of the incorporation of nitrogen into the products of photosynthesis such as the proteins and chlorophyll itself. In general, the nitrogen comes from nitrate or ammonium ions in the plant fluids fed to the leaf, but its incor-

#### FIGURE I - PRIMARY PHOTOSYNTHESIS REACTION

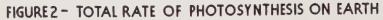


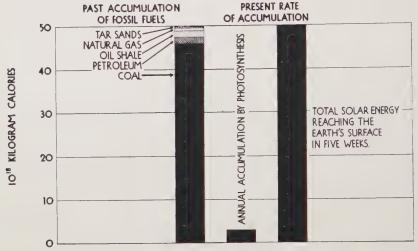
poration into the plant products may or may not be linked to a photochemical reaction.

The photosynthesis process has been a classical subject for investigation for at least 175 years. Generally speaking, in the early days, there was no real objective of the research beyond curiosity as to the workings of this important process and some desire to improve agriculture by increased knowledge of the photosynthesis reaction.

The objective of the Charles F. Kettering Foundation is to gain sufficient knowledge of the mechanism of photosynthesis that an identical or similar process can be developed outside the plant for use in the industrial production of food, fuel, or special chemicals. Our interest lies in the process of solar energy pick-up and conversion to chemical or electrical energy of high potential. The conversion of solar energy to low temperature heat for home heating, etc. does not provide a product capable of producing power and hence is of relatively limited applicability and interest.

Figure 2 shows how very ineffectively the Earth has been able to store the solar radiation incident upon it. The total amount of energy stored in the coal and petroleum in the Earth's crust during the past three billion years is only equivalent to the solar energy reaching the Earth's surface in five weeks! The rest of the incident solar energy has been re-radiated into space as low wave-length infra-red radiation. Some of it, of course, has been picked up temporarily by photosynthesis, and Figure 2 shows that the yearly accumulation of energy by photosynthesis is quite appreciable. However, decay of the plant material





allows this energy to be dissipated except for the infinitesimally small amount retained in the deposits which are being slowly made into peat and coal.

So it is seen that the Earth receives a tremendous amount of energy from the Sun which can be utilized to the extent that we learn how to use it. It is indeed a worthy challenge to the scientist and engineer. An inexhaustible source of energy or fuel is an objective worthy of great effort.

It is true that practically every major researcher in photosynthesis has a somewhat different approach to the problem. The study of chlorophyll has been a popular approach by many including the Kettering Foundation. Some of the most prominent people in the field are engaged in an effort to determine the "quantum efficiency" of photosynthesis,—the number of light quanta required to reduce one molecule of carbon dioxide. During the past five years, some interesting results have been obtained by feeding radioactive carbon-14 labeled carbon dioxide to plants exposed to light, killing the plants, extracting and identifying the intermediate products of photosynthesis. The results have not been as extensive as had been expected in the beginning, but advances have been made. However, no matter how successful the latter approach will turn out to be, little information will be gained as to the nature and mechanism of the most important portion of the process—the photochemical decomposition of water. Most authorities agree that the photosynthesis process can be divided into two separate parts (a) the photo-decomposition of water to release oxygen and form a reducing agent and (b) the reduction of carbon dioxide by the reducing agent without the aid of light. The labeled CO2 experiments will tend to FIGURE III - THE DEVELOPMENT OF THE PHO-TOSYNTHESIS PROCESS - A POSSIBLE TIME SEQUENCE

TIME

BEGINNING OF OCEAN CONDENSATION COOLING-OFF PERIOD OF THE EARTH

PERIOD OF ACCUMULATION OF ORGANIC MATERIALS

FIRST CATALYSTS (ENZYMES)

FIRST CELLS

FIRST UTILIZATION —
OF CARBON DIOXIDE

FIRST UTILIZATION OF RADIANT ENERGY

FIRST USE OF WATER AS REDUCTANT

FIRST DEOXIDATION
BY RELEASE OF
FREE OXYGEN

INDEPENDENCE FROM \_ ORGANIC SUBSTRATES DEVELOPMENT OF CATALYZED SELF-PERPETUATING REACTIONS USING ORGANIC MATERIALS FOR ENERGY AND STRUCTURE

DEVELOPMENT OF CHEMAUTO -TROPHIC ORGANISMS ~ ENERGY - OXIDATION OF INORGANIC

ENERGY-OXIDATION OF INORGANIC MATERIAL; STRUCTURE (CARBON) - CARBON DIOXIDE; REDUCTANT - INORGANIC MATERIAL

DEVELOPMENT OF PHOTAUTO-TROPHIC ORGANISMS ~

ENERGY ~ LIGHT STRUCTURE (CARBON) -CARBON DIOXIDE REDUCTANT - WATER, USING INORGANIC REDUCTANTS AS OXYGEN ACCEPTORS

DEVELOPMENT OF COMPLETELY PHOTOSYNTHETIC ORGANISMS~

ENERGY - LIGHT STRUCTURE (CARBON) - CARBON DIOXIDE REDUCTANT - WATER DEOXIDIZED BY RELEASE OF FREE OXYGEN

PERIOD OF INCREASING COMPLEXITY AND CHANGE TO MEET ENVIRON – MENTAL REQUIREMENTS

clarify the latter phase of the problem, but the photochemical reactions must be investigated in a different way.

The Charles F. Kettering Foundation program has been recently reorganized to concentrate on the photochemical phase of photosynthesis. Our overall approach to the problem we call the "prebiological" approach. As far as we know, in its overall

aspects it is unique.

Several years ago, Mr. Kettering formulated the basic principles of the "prebiological" approach when he thought about the generally held conviction that the photosynthesis process and apparatus in present-day green plants is the result of evolution from a much simpler process in the very early period of the existance of biological entities. By extending the idea to even earlier time periods, he realized the importance of conditions on the

## FIGURE 4 - THE DEVELOPMENT OF THE PHOTOSYNTHESIS PROCESS AN ALTERNATE POSSIBLE TIME SEQUENCE

TIME COOLING-OFF PERIOD OF THE EARTH **BEGINNING OF** OCEAN CONDENSATION FIRST UTILIZATION OF RADIANT ENERGY PERIOD OF "NON-PERPET-FIRST PHOTOLYSIS UATING" PHOTOCHEMICAL OF WATER **REACTIONS** FIRST REDUCTION OF CARBON DIOXIDE FIRST PRIMITIVE **ENZYMES** DEVELOPMENT OF CATALYSTS FIRST DEOXIDATION IN THE REACTING SYSTEMS BY RELEASE OF AND THE GRADUAL FORMA-FREE OXYGEN TION OF "SELF-PERPETUATING" SYSTEMS BEGINNING OF PHOTOSYNTHETIC PIGMENTS -PHOTOCHEMICAL CATALYSTS (UTILIZATION OF VISIBLE SPECTRUM) DEVELOPMENT OF SELF-CON-FIRST CELLS TAINED, "SELF-PERPETUATING" SYSTEMS

Earth and sequence of events leading to the formation of the first biological cells. This period in history he called the "prebiological" period, and the corresponding chemical and physical events he call "prebiological chemistry and physics." A knowledge of the "prebiological" period and of the first part of the subsequent "biological" period would be of immense value in unraveling the photosynthesis tangle. Obviously, an exact knowledge of the prebiological period is impossible, but it does seem possible to use indirect evidence to build up a hypothetical picture which could be very useful, of the prebiological period and its sequence of events. This we are endeavoring to do, with moderate success to date.

Figure 3 shows a possible time sequence of events by which cells capable of photosynthesis could have been evolved. This particular sequence is a summary of ideas of several authorities and probably represents the feelings of most biologists. It assumes that the utilization of solar energy followed the use of energy from the oxidation of available high energy matter.

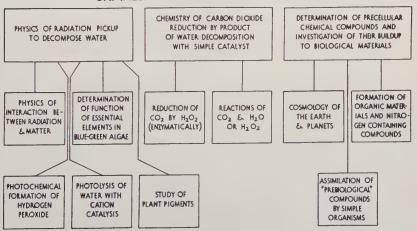
Figure 4 shows an alternate time sequence in which it is postulated that the radiation from the sun was the actuating energy from the very beginning and that biological cells using energy from the oxidation of carbon and hydrogen compounds

were later developments.

The latter supposition is quite logical in many ways, and we tend to favor it over the former sequence. However, neither sequence may even approximate the actual series of events.

Figure 5 is a summarized chart of the main portions of the Foundation's photosynthesis research program. As can be seen, the program can be divided into three main avenues of attack—the physics of radiation pickup, the chemistry of carbon dioxide

## FIGURE 5-OUTLINE OF RESEARCH PROGRAM CHARLES F. KETTERING FOUNDATION



reduction, and the investigation of prebiological chemistry. The

emphasis is on the first category.

Figure 6 is a list of molecules and compounds that we believe to have been present at the surface of the Earth during "prebiological" times. Only the more obvious materials are placed under the category "definite." Most of the other compounds have been added to our list from literature research and our experi-

#### FIGURE 6 - PREBIOLOGICAL COMPOUNDS

# DEFINITE H<sub>2</sub>O CO<sub>2</sub> O<sub>2</sub> O<sub>3</sub> N<sub>2</sub> NH<sub>3</sub> H<sub>2</sub> HNO<sub>3</sub> H<sub>2</sub>O<sub>2</sub>

## PROBABLE ACETYLENE GLYCINE ALANINE CARBON CARBON MONOXIDE HCN HCNO OXALIC ACID FORMIC ACID OXAMIDE "AZULMIC ACID" CYANOGEN UREA METAL CARBIDES

## PYROLLE FORMALDEHYDE HYDROCARBON MIXTURES

## FIGURE 7 -SOURCES OF PREBIOLOGICAL ORGANIC COMPOUNDS THE HYDROLYSIS OF CYANOGEN

1) LIQUID PHASE

$$N = C$$
 $N = C$ 
 $N$ 

mental investigations in the Chemistry Department of the Ohio

State University.

For instance, there is reason to believe that cyanogen would have been present in the prebiological atmosphere. The hydrolysis of cyanogen yields many biologically interesting substances, a few examples of which are given in Figure 7.

The hydrolysis of metal carbides probably furnished many organic compounds. Figure 8 shows several examples of known

### FIGURE 8 - SOURCES OF PREBIOLOGICAL ORGANIC COMPOUNDS THE HYDROLYSIS OF CARBIDES

1) 
$$AI_4C_3 + 6H_2O \rightarrow 3CH_4 + 2AI_2O_3$$
  
ALUMINUM CARBIDE WATER METHANE ALUMINUM OXIDE

2) 
$$3 \text{ Fe}_{\text{m}} \text{C}_{\text{n}} + 4 \text{m} \text{ H}_2 \text{O} \rightarrow \text{C}_{3 \text{n}} \text{H}_{8 \text{m}} + \text{m} \text{Fe}_3 \text{O}_4$$

IRON CARBIDE WATER NAPHTHA IRON OXIDE

3) 
$$C_{\alpha}C_{2} + H_{2}O \rightarrow HC \equiv CH + C_{\alpha}O$$

CALCIUM CARBIDE WATER ACETYLENE CALCIUM OXIDE

 $HC \equiv CH + H_{2}O \xrightarrow{300^{\circ}C} HC - C = O$ 

ACETYLENE WATER ACETALDEHYDE

### FIGURE 9 - SOURCES OF PREBIOLOGICAL ORGANIC COMPOUNDS

reactions which could have been involved. The presence of nitrogen containing compounds could be explained by such known

reactions shown in Figure 9.

The radiation from the Sun is converted to other forms of energy on the Earth's surface in the four main ways listed in Figure 10. By the evaporation of water, water vapor enters the atmosphere and is carried above the mountains. Rain falls and rivers flow downward toward the sea. By proper placement of dams and powerhouses, some of the potential energy in this water can be converted to useful electrical energy. The use of solar energy for space heating has been mentioned previously. It is possible, but only barely practical under favorable conditions, to use solar energy to heat boilers for steam power generation.

Atmospheric electricity is generated as an indirect result of the solar evaporation of water into clouds. This electric energy

cannot be utilized effectively.

By far the largest amount of solar energy conversion takes place in green plants, where water is decomposed in photosynthesis, and the energy thus trapped is used to form plant products such as carbohydrates, fats, and proteins from carbon dioxide. This was the original source of the energy we obtain when we burn coal or petroleum products. Such a process is one we wish to duplicate or improve.

Chlorophyll has been mentioned as the most probable agent of radiation reception in the green plant. It may not be the only one, however. Chlorophyll can be extracted from green leaves or other green portions of plants by organic solvents. Its structure has never been completely confirmed as it has never been synthesized. Figure 11 shows the structure most generally considered correct. However, there is evidence to indicate that chlorophyll

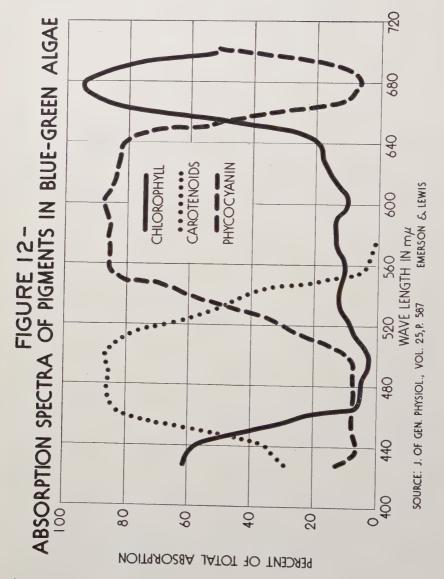
### FIGURE 10 - RADIATION FROM THE SUN

- I ~ EVAPORATION OF WATER
- 2 HEATING THROUGH SURFACES
- 3 ~ GENERATING ATMOSPHERIC ELECTRICITY
- 4 ~ DECOMPOSITION OF WATER (THE BASIS OF PHOTOSYNTHESIS)

exists in the plant as a complex with protein. It has been shown many times that extracted chlorophyll is unable to produce photosynthesis outside the plant thus tending to confirm the fact that the protein complex is required in the plant for proper functioning.

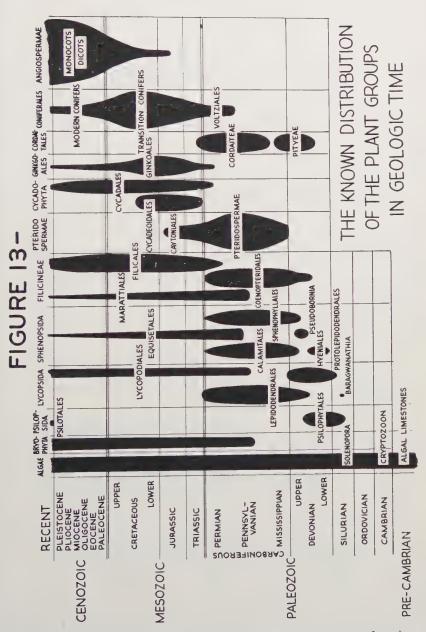
Chlorophyll is not the only pigment present in photosynthesizing plants. Most plants have 3 or 4 other pigments, depending on the type of plant. For instance, most blue-green algae, simple single cell plants, have a water-soluble blue pigment, called phycocyanin, plus one or more carotenoid pigments. The absorption curves for a typical set of these pigments is presented in Figure 12. It is interesting to note that the sum of the per cent absorption is about 100 over the entire visible spectrum. Chlorophyll itself absorbs light appreciable only in the red and violet regions. From the curves in Figure 12, it would appear that practically all incident visible light is absorbed by the pigments in blue-green algae. Whether light over the entire visible spectrum is used in photosynthesis is somewhat doubtful. The green color of leaves, green algae, etc., is due to the fact that light in the green region of the spectrum is not absorbed appreciably and hence is reflected preferentially.

The blue-green algae were selected as objects of experimentation because they are generally considered to have been derived directly from the earliest photosynthetic plants without appreciable change. A generalized distribution of plant group development during the geological periods is shown in Figure 13. Traces of algae are found in the Pre-Cambrian rock, the oldest rock found on the Earth's surface. However, bacterial traces are also



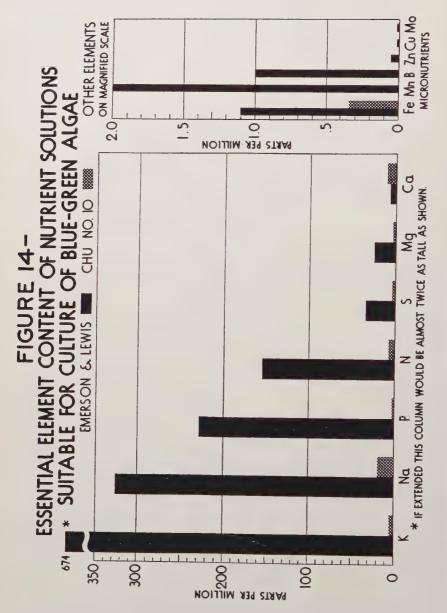
found in rock of the same age, so geological evidence is not sufficient to settle the point as to whether the photosynthetic plants preceded the hetrotrophic plants in the evolutionary sequence or vice versa.

We are culturing several species of blue-green algae, both fresh-water and marine, in an effort to determine (a) the elements essential to this growth, and (b) the functions of the elements. Neither investigation is particularly easy to do, al-



though modern techniques in analyzing for and removing trace The determination of the function of elements are very helpful. the various elements will be comparatively difficult to achieve and complete success within a short period is doubtful.

It is believed that one or more of the elements in the algae



nutrient solutions are active in the photosynthesis process, and our algae researches are aimed at determining just which element or elements is involved. The program consists initially of growing algae in flasks of inorganic salt nutrient solutions deficient in various elements. The composition of the two most commonly used nutrient solutions for blue-green algae are shown

in Figure 14. Note that there is very little similarity either in total amounts of each element or in their ratios. Both nutrient solutions have a pH which is slightly on the alkaline side as the blue-green algae do not grow well in acid solution. We believe that the pH is of primary importance and that as long as all the elements necessary are present, the concentration of each is relatively unimportant as long as toxic amounts are not reached.

However, the list of elements generally considered essential to the higher green plants, is not complete, at least not for the blue-green algae. We have shown this to be true by making up nutrient solutions with only the known essential elements added. By repeated series of subculturing we have found that the amount of total growth of algae in each new subculture tends to grow less for a while and then reaches a relatively weak steady amount. We interpret this as meaning that impurities furnish a certain amount of all the essential elements but if every essential element were added in reasonable quantity the growth would have been heavy. When nutrient solutions are inoculated from a few cells from an agar slant the growth is always heavy, probably due to the large amount of the trace elements picked up and stored by the cells when growing off the agar slant. Agar contains a large number of elements as impurities, and these no doubt become available to the cells as they grow in contact with the agar.

Some recent work in the Chemistry Department of the Ohio State University under the Kettering Foundation sponsorship has given some evidence that hydrogen peroxide may be the important reducing agent formed by the photodecomposition of water and hence the intermediate capable of reducing carbon dioxide in the plant. Hydrogen peroxide usually acts as a rather powerful oxidizing agent, but in certain cases it can be a reducing agent. This property is due to the tendency for the extra oxygen atom in hydrogen peroxide to unite with an oxygen atom in the other compounds to form  $O_2$  gas. The net effort is the reduction of the other compound.

We are placing the emphasis of our research program at present on the following:

(a) The formation of H<sub>2</sub>O<sub>2</sub> from water by light in the presence of ZnO or other catalysts.

(b) The photochemical decomposition of water by light in the presence of inorganic cations such as ferric-ferrous.

(c) The physics of the interaction between radiation and matter.

The above description of the photosynthesis research program of the Charles F. Kettering Foundation is of necessity quite condensed and simplified. However, the basic "prebiological" approach was explained in some detail, and it is this approach that we are hoping will yield practical results within the next few years.



A. L. LANG

Prof. Lang was born September 7, 1896, at Dilsboro, Indiana. He graduated from the University of Illinois in 1920 and from Cornell University in 1929. Since his graduation from Illinois he has given practically all of his time to an intensive study of Illinois soil fertility problems with the exception of that spent in graduate work at Cornell. This largely has been concerned with the great number of investigational centers systematically arranged over the State of which he is now in charge. These include the classical fertility plot studies located at Urbana which are now among the oldest continuing investigations of this nature in existance.

## THE USE OF ROCK PHOSPHATE IN ILLINOIS DURING AND SINCE THE TIME OF HOPKINS

#### A. L. LANG

#### Introduction

In order to do justice to my subject I shall review briefly the early literature related to soils work of the Illinois Experiment Station. This review is not intended to eulogize, but it is an attempt to put in writing what I believe are important facts and as

I think they ought to be recorded.

Only those who studied under Hopkins or who have taken time to read his literature intimately can have any conception of his thinking. It seems fitting, therefore, after 50 years that his guiding principles, formulated at the very beginning of his work, be reviewed and again recorded. The sincere belief of Hopkins in the absolute necessity for preservation of soil productivity and a demand from his superiors for a permanent system of agriculture led to his conception of the Illinois System of Permanent Soil Fertility. Into this system he incorporated the use of crushed limestone from vast local deposits, finely ground unacidulated rock phosphate direct from mine to farm, farm-produced residues as a source of organic matter and potash and free legume nitrogen from the air.

A short discussion of the system will be given to make the fundamental principles involved more clearly understood. Then information which has a bearing on the use of rock phosphate in

the system will be presented.

#### EARLY HISTORY

Up to 1900 Illinois lagged far behind her sister states in making facilities available for teaching and investigating agricultural subjects. The first soil experiment plots established were not designed to study soil improvement, but rather to demonstrate soil depletion. I refer to the Morrow plots started in 1876. They are still being maintained and are serving their purpose well. Not until 1904 were portions of these plots utilized for soil improvement practices.

Beginning in 1879 with enactment of the Hatch Act, carefully conducted experiments with fertilizing materials applied directly for grain crops showed no appreciable benefits from such practices. Only good effects of animal manures and turned under clover meadows seemed worthy of note. I bring this in to point out that even before the turn of the century fertilizing

individual crops did not appear practical in Illinois. But a hazy conception of soil care as a function related to soil rather than

crop culture was slowly developing.

During this early period, President Draper of the University probably pulled the prop that launched the boat when he pronounced the often quoted adage, "The wealth of Illinois is in her soils and her strength in their intelligent development." This statement was undoubtedly a challenge to Davenport, Director of the Experiment Station, and to Hopkins. It is still a challenge to all of us.

The members of the Illinois State Farmers' Institute, an organization which came into being by an act of the Illinois legislature in 1895, probably had more influence on early agricultural education and research programs of the state than any other person or body of people because from the time of inception its members took responsibility for sponsoring appropriations for such activities. Many members were the first to put into practice and demonstrate the practicability of findings and teachings from such research. Such men as Mann, Allen, Abbott, Wilson, Hinkley, Meis, and many others will long be remembered as contributors in this way. However, it is very evident that members of this organization were first inspired through efforts of Davenport, and then later by Hopkins and his co-workers. Addressing the second annual meeting of the Institute February 23, 1897, Davenport kindled members of that organization into action by revealing history of the scourge of soil depletion and its effect on past civilization. In that address he made these significant statements: "With all our boasted knowledge of agriculture, we cannot today with confidence lay down practices that will be safe and profitable and that will sustain productive capacity of these prairies for 1,000 years. I say without fear of contradiction, our race does not know how to do it." He further stated, "This is a problem whose solution we cannot too soon begin if we feel a racial pride and would do our duty to posterity."1

In the statements of Draper and Davenport we see need and administrative demand for a permanent system of soil preservation. In 1900, largely through efforts of the Farmers' Institute, the State Legislature appropriated money for the most commodious agricultural building then in existence, and the following year in 1901 under the same influence the legislature appropriated \$10,000 for the purpose of soil investigations. Investigation started by that appropriation and continued by subsequent and larger ones have been largely responsible for continued widespread use of rock phosphate.

#### HOPKINS

Cyril G. Hopkins was made head of the Department of Agron-

<sup>1-</sup>Report, Illinois Farmers' Institute, Volume 2. 1896.

omy and given a first chair in Agronomy at the University of Illinois in 1900. He was an untiring worker with a keen mind and an art of sifting important from unimportant facts. In a short span of time he accumulated known facts of agriculture from all over the world and made widespread practical applications of his findings.

With the first appropriation from the legislature in 1901 made available for the specific purpose, Hopkins launched a state-wide program of soil investigations. Hopkins himself maintained until the last that Davenport was responsible for their inception.<sup>2</sup> Anyway, the scope, intensity, and continuity of these investigations have never been equalled before or since. There were 3 objectives set up.<sup>3</sup>

First, to determine the stock pile of total plant food in the most extensive soil areas of the state by collecting and analyzing soil samples.

Second, to determine the productive capacity of different soil treatments and different plant foods in terms of crop yields by means of controlled greenhouse pot culture and extensive field experiments.

Third, to locate boundaries of the most extensive soil areas and minute soil types in the state by first making a hurried general survey followed by a detailed survey down to each 10 acres.

With exception of the first part of this program the original plan is being continued almost in its entirety 50 years after its inauguration. Here it is worthy of note that Hopkins himself acquired most of the analogies of which he taught and wrote in respect to the fundamentals of permanent soil fertility from findings of chemical analysis in the early part of his investigations. Hopkins used experimental data furnished him by investigators in other states and countries to confirm his own convictions before his own data were available for that purpose. From his early publications it is evident that Hopkins had a clearly defined system of permanent soil fertility in his mind at the beginning of his investigations. At the annual meeting of the Illinois Farmers' Institute in 1903 Hopkins stated, "There is but one answer to the question of maintaining the fertility of all the soils which have been ruined in the past ages. This is the answer. Preserve good physical condition, put back on the land all the fertility which is taken off, not some of it, not most of it, but all of it and not only that which is removed by cropping, but also that removed by blowing, washing or leaching of the soil."4

Along with this pronouncement he offered five rules for improving soils and feeding plants. They are:

<sup>2-</sup>Illinois circular 157, March 1912, page 14.

<sup>3-</sup>Illinois circular 64, 1903.

<sup>4-</sup>Illinois circular 68, pages 2 and 3, April 1903.

- 1. If soil is acid, apply lime.
- 2. If soil is poor in nitrogen, grow clover.
- 3. If soil is poor in phosphorus, apply bone meal or some other source.
- 4. If soil is poor in potassium, apply potassium chloride or some other material containing potassium.
- 5. Always save all animal manures and make liberal use of green manures.

Following this, Hopkins stated that only three forms of phosphate should be considered for use in Illinois. These are:

1. Finely ground bone.

2. Finely ground rock phosphate.

3. Finely ground basic slag.

This may have been his first public announcement on rock phosphate. In supporting this statement he reports significant data from both Ohio and Maryland having to do with the carriers of phosphate and makes this statement, "All of these experiments strongly indicate that finely ground rock phosphate as well as bone meal will be a valuable form of phosphorus to use in Illinois." This is interesting in light of the fact that only one year before 15 soil experiment fields has been established on which bone meal was used exclusively as a source of phosphorus. There is no doubt that during the early part of his career Hopkins garnered most of his facts from statements by workers of other states. He acknowledges this later in his writings and takes no credit for establishing the fact that rock phosphate was a good source of phosphorus for direct application.

One example will serve to illustrate this point. Director Thorne of the Ohio Agricultural Experiment Station spoke on the same Illinois Farmers' Institute program with Hopkins in 1903. At this meeting in commenting on the increase of wheat yields in Ohio over a 50-year period, he said, "It has nevertheless been accomplished at so large an expenditure for commercial fertilizers as to leave it open to question whether there has been an actual gain. The result is that our fertilizer costs have run up to an average of more than a million and a half dollars annually, about one-third of which we pay for being persuaded to buy. Let me not be understood as condemning the use of fertilizers. On the contrary, I regard the utilization of the great deposits of phosphate rock, nitrate of soda, potash salts, and the waste from our slaughter houses as one of the greatest steps in modern agricultural progress. When blind, haphazard use of these materials takes the place of an intelligent study of the fundamental principles of agriculture as it too often has been done in Ohio, they become a curse instead of a blessing." Later in the same paper, Director Thorne states that a ton of stall manure was increased in value from \$2.50 to \$3.25 when 40 pounds of phosphate rock was added to each ton for the purpose of re-inforcing the manure with phosphoric acid and preventing the escape of ammonia.<sup>5</sup>

Many remember Hopkins only as the great proponent of rock phosphate. This is unfortunate because it does an injustice to his teachings to present science and the rock phosphate industry. The facts reveal that Hopkins 50 years ago was more nearly aware of the great need for nitrogen and potassium fertilization than many present day agronomists. His great quarrel with the fertilizer industry had to do with the lack of proper nutritional balance and costs that made adequate application unattainable.

To meet adequately the demands of crops for nitrogen Hopkins recommended and used in his early experiments 100 pounds of nitrogen annually. This makes pikers out of most of us. His work demonstrated the crying need of crops for nitrogen and pointed to the great deficiencies in the seemingly fertile Illinois prairie soils. Furthermore, the work demonstrated the utter impossibility of ever supplying this enormous need through commercial channels. Widely distributed experiments over the entire country are still demonstrating these glaring facts. At present, favorable price ratio between nitrogen fertilizers and farm crops offer a great opportunity for using large quantities of commercial nitrogen. (Unfortunately supplies are relatively scarce.) Even as most agronomists today are doing, Hopkins concluded that legumes would have to be relied upon as the major source of this important nutrient. Hence the soil management problem resolved itself into one of growing legumes. Legumes to be grown in Illinois required large quantities of limestone and much more phosphorus than the soils could supply. Since phosphorus in the available sources of mixed fertilizers was far too costly to encourage adequate applications for maximum legume production, and since legumes had demonstrated their ability to utilize phosphorus from rock phosphate, Hopkins saw in this source a means of getting the job done. This logic is still good.

#### THE ILLINOIS SYSTEM OF PERMANENT SOIL FERTILITY

Out of all this came the Illinois System of Permanent Soil Fertility in which rock phosphate has a part. It is a plan of soil management recommended for building up and maintaining permanent productivity. The objectives of the plan are to keep soil physically fit, chemically balanced, and biologically active. Fundamental to the plan are recommendations by which the objectives are accomplished. Herein controversies arise as would be expected when dealing with the many ramifications brought about by forces of man and nature on a dynamic, biologically active medium such as the soil. Principles underlying recommendations in the system result from an economic analogy relating long-time average agricultural incomes in the Corn Belt to

<sup>5—</sup>Illinois Farmers' Institute report, 1903.

possibilities of getting the job done. This analogy was based on existing facts which are as true today as when they first were

pointed out. These were:

1. Cultural practices used in general agriculture were exploitive. "Tickle the earth with a hoe and she laughs with a bountiful harvest. When the tickling fails to produce, new fields to impoverish are sought, and westward the course of empire takes its way, with ruined lands behind." That was the song of the prairies.

2. Exploitation could not continue if civilization and a free

people were to survive.

3. Incomes from general farming practices were relatively low. For example, from 1900 to 1911 the average prices in the Corn Belt were 70 cents for wheat, 35 cents for corn,

25 cents for oats and \$6.00 a ton for hay.

4. Commonly recommended fertilizer practices were too costly to encourage adequate applications. Phosphorus in the most common fertilizer, 2-8-2, costs 30 cents a pound. The potash in such a fertilizer would dilute an Illinois soil. Costly burnt limestone was being recommended as a source of lime for correcting acidity and furnishing calcium.

To meet the challenge of soil exploitation in the midst of adversities of low income and costly replenishment, Hopkins reasoned that Illinois farmers could use larger quantities of less expensive crushed limestone from vast local deposits, legume nitrogen free from the air, inexpensive untreated rock phosphate and could make judicious use of all farm-produced residues for organic matter and for liberating a much needed and abundant supply of potassium from the soil.

In that reasoning is embodied the basic principle underlying the Illinois System of Permanent Soil Fertility. Furthermore, those are the principles which from the beginning have kept our research work and our extension teachings on a straight, definite, systematic, simple, easily understood, easily applied, and workable soil improvement program. There have been no byways, and no tangents, no delays, but a constant forward effort to improve on, add to and compare.

#### WHY ROCK PHOSPHATE?

From his own analogies Hopkins reasoned that phosphorus was the key to permanent agriculture. With \$1,000,000 worth of nitrogen over every acre of the land and available to the soil through legumes, he argued that Illinois farmers need not buy a pound of that most important nutrient. Likewise, with enough potash in each acre of land to last for 19 centuries he maintained that some system should be used to make it available, thereby avoiding purchase from outside sources. Phosphorus, however, was different. Surface soils showed only enough total phosphorus

to last one man's lifetime. Hence, if permanent fertility was to be maintained this essential nutrient would have to be purchased and returned to the land from outside sources. Also it would have to be returned in proportion to that taken from the land through cropping, wind erosion, leaching, and washing. Bone meal, basic slag, rock phosphate, and superphosphates were on the market in the early days as they are today. Hopkins contended that bone meal was the ideal source of phosphorus for Illinois farm land, because it was a farm product, and its return to the soil tended toward a permanent cycle. He pointed out, however, that its cost discouraged the use of maintenance quantities. Likewise, price was unfavorable to basic slag and acid phosphates, therefore, rock phosphate costing only \$7 to \$8 a ton delivered to Illinois farms offered the more ideal source of phosphorus for this purpose.

Thus Hopkins set out to learn about rock phosphate, and he gathered together in detail all of the available experimental evidence on the subject of phosphatic fertilizers. His interpretations of the many long-time experiments which preceded by far his own research work are available in the many early circulars of the Illinois Station. Briefly it was the long-time experiments from Maine, Massachusetts, Maryland, and Ohio that in the mind of Hopkins established beyond a doubt that rock phosphate was the most economical source of phosphorus for use in permanent systems of soil fertility maintenance.

From this acknowledgment Illinois cannot claim credit for first establishing the fact that rock phosphate was an economical source of phosphorus for permanent systems of agriculture. Many times in his early teachings, Hopkins pointed out that the famous old manure experiments at Ohio comparing rock and acid phosphate were the World's greatest contribution to Illinois farms. In the beginning of those experiments, both Director Thorne of the Ohio Station and Hopkins interpreted them as favoring rock phosphate. Later, however, their interpretations became a controversial matter and Hopkins stayed on the rock phosphate side.

Hopkins maintained there was little use of further study on the matter of phosphate carriers. For Illinois the problem was settled. Consequently, since 1903 rock phosphate has been the main source of phosphorus for farm use and for all major ex-

periments in the state.

According to Hopkins the first carloads of rock phosphate purchased in the state were probably used for experimental work. However, the records show that in 1903, A. A. Hinkle of DuBois purchased 1½ cars of rock phosphate. This may be the first record of its farm use in Illinois. His results and those of the experiment fields were so encouraging that its use spread rapidly

<sup>6—</sup>Illinois circulars 86, 96, and 97 and Illinois bulletin 99 are most important.

Table 1 .-- ILLINOIS SOIL EXPERIMENT FIELD DATA Average Annual Acre Values, 1946-1949

						Current Farm Prices	rm Prices	:		
		Check	M	L/M	Increases P/ML	MLP	P/ML MLP L/O P/L	ractices P/L	K/LP	I.PK*
I,	Aledo	\$63.20	\$22.26	\$ 3.73	\$-1.29	\$24.70	\$11.71	\$ 2.36	\$ .58	\$14.65
II	Hartsburg	76.43	28.23	2.07	.38	30.68	7.16	2.48	03	9.61
	Minonk	71.49	14.63	72	-3.04	10.87	1.34	4.14	.23	5.71
III	Kewanee	52.72	19.55	4.36	86	23.05	11.25	2.32	-3.99	9.58
14	Dixon	57.96	25.74	7.43	.78	33.95	12.58	6.20	4, 38	23.16
	Mt. Morris	41.86	56.46	8.09	32	34.23	27.77	3.60	-3.10	28.27
Δ	Carlinville	50.74	26.72	19.26	7.27	53.25	19.28	9.87	69.6	38.84
	Carthage	58.95	21,59	8.03	1.63	31.25	11.66	.19	2,45	14,30
	Clayton	54.43	21.29	6.85	1.90	30.04	10.56	4,80	- 36	15.00
	Lebanon	54.09	45.06	14.14	-1.67	54.53	29.82	1.54	10,38	41.74
ΔĪ	Joliet	49.39	17.22	2.06	10.33	29.61	3.11	14.90	3.87	21,88
VII	Ewing	20.42	15.21	29.01	6.25	50.47	10.18	6.82	30.54	75 27
	Newton	15.35	17.03	34.22	4.51	55.76	21,89	5,14	10,36	37,39
	Oblong .	29.43	20.23	26.57	3.53	50,33	16.00	5.69	20.75	47.74
	Toledo	23.19	24.11	19.80	57	43.34	15.53	.63	29.14	45.30
M	Enfield	15.75	17.39	25,20	6.24	48.83	16.17	6.71	9.43	32.31
	Raleigh	15.55	10.75	23.64	.77	35.16	11,85	6.32	11.77	29,94
	Sparta	7.47	9.39	35.00	2.17	96.94	27.40	1.16	17.67	46,23
XIV	Oquawka	18.07	9,62	19.14	19	28.57	16,50	.23	10.19	26.92
XVI	Elizabethtown	9.98	19.77	21.05	8.19	49.01	18,42	12,64	8.58	39.64
	Average	\$39.32	\$20.46	\$15.45	\$ 2.30	\$38.21	\$15.01	\$ 4.89	\$ 8.63	\$28.52
Ψ.	manure - equal in weight to crops removed	weight to	crops remo	oved					cost	5.25
11	limestone - equivalent to approximately 500 pounds annually	lent to ap	proximatel	y 500 pour	ids annuall	Δ.			diff.	\$23.27
1	rock phosphate - equivalent to approximately 200 pounds annually	quivalent	to approx1	mately 200	pounds an	nually				

\*Does not include value of residues returned without treatment. This would average 8 to 10 dollars annually.

K - potassium chloride - equivalent to 100 pounds annually Values - Current prices received each year at the farm.

throughout the state and has continued from that time on. It is estimated that approximately 27,000 tons were used from 1903 to 1920, during which time there is no official record. Since 1920 Illinois has used 3,670,422 tons. The trend has been constantly upward. The peak of use was reached in 1947 when more than 600,000 tons were applied to Illinois farm lands. That figure along with  $P_2O_5$  supplied in mixed fertilizers and superphosphate enabled us to say that Illinois was applying more phosphorus than any other state in the United States. This could not have been accomplished during or following a wartime emergency without our rock phosphate program.

#### A FEW FARMER EXPERIENCES

From the very beginning, farmers themselves were the most enthusiastic supporters and promoters of the system. There are the printed statements of such men as Brother Leo, long-time manager of the Notre Dame 1,000-acre farm at South Bend, Indiana, Frank I. Man, Gilman, Illinois, records of Hopkins own "poorland farm," Salem, Illinois, Allen Meis, Hinkley, and many others.

Records of the Farm Bureau-Farm Management Service are the best source of information on present day accomplishments. The Farm Bureau-Farm Management Service is a cooperative management service between farmers and the Agricultural Economics extension staff. The field technicians paid by the farmers aid in the keeping of exacting records of the farms' enterprises. Professor M. L. Mosier of the Agricultural Economics staff at the University of Illinois in summarizing long-time records from these farms revealed that farmers putting into practice recommendations of the experiment station have equalled or bettered results of field research findings. The records proved beyond any doubt that some Illinois farms can average and have averaged more than 100 bushels of corn an acre on their entire farm in good years and over a period of years.<sup>10</sup>

## RESULTS FROM FIELD EXPERIMENTS SHOW HOW FARMERS BENEFIT

A summary of the yield on the bases of current farm prices for long-time or rotation periods brings out noteworthy information. The following data from Table 1 is an analysis of figures from the last rotation period on 20 outlying soil experiment fields.

These show that organic matter either as animal manure or crop residues has been the most important factor in increased

<sup>7—</sup>Illinois circular 186.

<sup>8-</sup>Illinois Farmers' Institute Report, 1911, page 95.

<sup>9-</sup>Illinois circular 168,

<sup>10-</sup>Illinois News Release, 1950.

crop production. Values given to other soil amendments largely measure their ability to produce organic matter which can be returned to the soil.

Interpreted this way, limestone has returned more per dollar invested than any other soil amendment. Largely because of these facts Illinois farmers have been induced to use about one sixth of all the lime used in the United States and have profited handsomely by it. We think it is very fortunate in Illinois that the lime program has not been overshadowed by more glamorous but less profitable practices.

Rock phosphate on the ten fields where phosphorus has been profitable to use in addition to limestone and manure has returned \$4.00 per dollar invested.

Rock phosphate and potash in combination over lime on 12 fields where both are needed has returned more than \$5.00 per dollar invested in the two.

As an average on all fields limestone and rock phosphate have returned annually \$17.75 an acre over manure. In grain systems, limestone, rock phosphate and potash have returned \$28.52 an acre annually.

The annual acre cost of the limestone, rock phosphate and potash in the grain system of farming has been \$4.50 and the annual return per dollar invested has been more than \$6.00.

These are the kinds of facts and figures that keep up our enthusiasm.

#### PROGRESS

Some will ask, "How much progress has been made since the time of Hopkins?" The answer is much. It can be substantiated. But if none had been made I feel I am safe in saying for the field research staff that we are proud of the fact that we have carried on. To hold the line against the pressure of opposition with glamorous proposals has not been easy for a young college staff who are ambitious and trying to make reputations. You can recall that it was a completely new and young staff that took over the agronomic work at Illinois when Doctor Hopkins was called from it.

For the continuity of the work, Dr. W. L. Burlison, who carried the responsibility as head of the department, deserves more credit than history will record. Even though from the beginning of his administration pressure has been constantly on him to discontinue much of the work started by Hopkins, he has held steadfast. Convinced that it was right, he has been willing to see the work of his predecessor carried on successfully rather than to launch out on a new program of his own.

Illinois is perhaps as fortunate to have had a Burlison as it was to have had a Hopkins. But for Burlison the entire efforts of Davenport, the Illinois State Farmers' Institute, and Hopkins

might have been pushed aside and lost. We could have and still can degenerate into a blind haphazard unscientific use of plant food materials as condemned by Thorne 40 years ago. May we be blessed with leadership during the next 50 years as strong as that which we have had during the past.

#### EXPERIMENTAL EVIDENCE

From the very beginning the benefits to be derived from the use of rock phosphate in Illinois have been supported by experimental field data.

The Muscoutah Field in St. Clair County which was operated from 1904 to 1913 furnishes data given in Table 2 which is typi-

TABLE 2.—MUSCOUTAH FIELD 1904 to 1913

Crop	Corn	Oats	Wheat
No. of Crops	8	4	
	bu.	bu.	bu.
Check	39	33	23
Acid Phosphate	42	40	25
Rock Phosphate	46	38	26

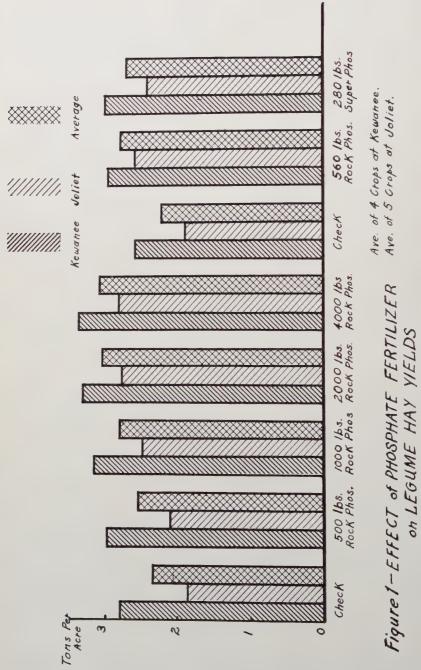
Initial application 400 pounds of acid phosphate. 1,000 pounds of rock phosphate with continued 200 pounds of acid and 500 pounds of rock each rotation.

TABLE 3.—LIMESTONE, ROCK PHOSPHATE, SUPERPHOSPHATE COMPARISONS ON 14 OUTLYING ILLINOIS SOIL EXPERIMENT FIELDS.

Averag	e annu			ops on th		on figures	
		at cu	irrent far	m prices.			
		ML	MLrP	MLsP	LeL	LeLrP	LeLsP
Aledo	27	54.02	54.41	54.47	45.80	46.91	45.87
Antioch	26					25.43	25.95
Bloomington	26					41.43	40.82
Brownstown	11					32.27	35.27
Carthage	22	44.15	44.40	44.74	38.16	40.34	40.10
Dixon	27	44.93	45.28	45.65	37.27	39.80	39.67
Ewing	22	34.61	36.80	35.80	24.68	33.15	31.06
Hartsburg	27	49.33	50.63	50.04	41.74	44.88	45.35
Lebanon	22	50.47	50.74	49.15	43.37	43.88	42.58
Minonk	11	67.80	66.80	68.50	56.32	59.87	59.86
Oblong	12	53.43	56.09	56.93	45.88	50.10	47.19
Raleigh	27	23.74	26.65	26.33	15.74	20.44	20.45
Sparta	21					27.10	26.95
Toledo	$\frac{21}{21}$		37.86	39.38		34.72	34.32
101040							
Average			45.34	45.33		37.54	37.17

Lime is applied to give a range of pH 6 to 6.5.

Phosphates on most fields have been applied at approximately equal money values.



cal of some of the early comparisons on phosphate carriers. Like that of other fields the data from Muscoutah show that rock phosphate is an effective source of phosphorus when compared to superphosphate.

Since 1924 the present experimental field staff has been trying to accumulate more and more evidence on the relative merits of rock and superphosphate. At present almost every experimental field has work going on which contributes information on the subject. All of these data, however, have not lessened the enthusiasm for rock phosphate.

It has been found generally that when rock phosphate is not effective superphosphate is likewise ineffective. The exception to this is in high lime soils above pH 7.

Fourteen fields give an opportunity to compare rock and super over a long period of years when used in most cases at approximately equal money values. A summary is given in Table 3.

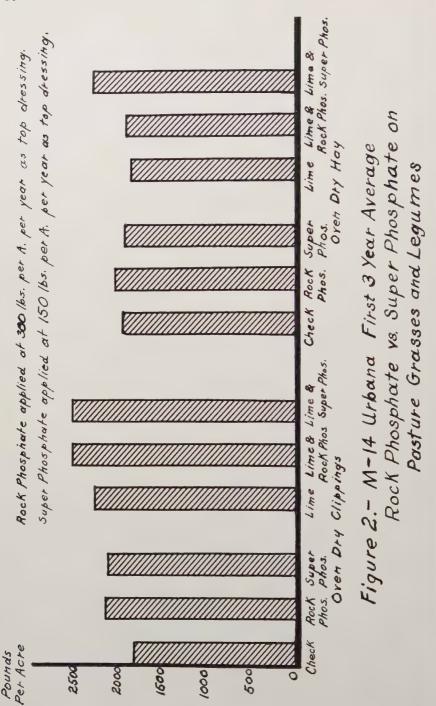
Some interesting data on rates of application of rock phosphate and comparisons with rock and super have been secured at Joliet and Kewanee. These data are shown in Fig. 1. From this work it appears that the law of diminishing returns on initial applications is somewhere between 1,000 and 2,000 pounds of rock phosphate an acre. This varies with soil type and phosphorus deficiencies. There was about equal response to each of the carriers when used with the legumes at equal money value.

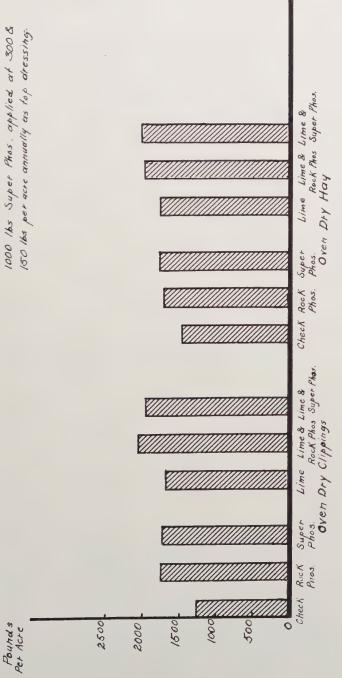
At Urbana rock and superphosphate were compared at equal money values when top-dressed on permanent pasture sods at relatively small amounts annually over a period of 10 years. The results for the first 3 years are shown in Fig. 2 and for the entire period in Fig. 3.

The comparative value of rock and superphosphate was measured by Professor L. B. Miller of the field staff in semi-permanent cooperative experiments with farmers over a period of 12 years. The carriers were applied at equal money value and their values measured in corn yields. An analysis of the data given in Fig. 4 shows several possible advantages in the use of rock.

- 1. More phosphorus was applied to the soil.
- 2. More was removed by the crop.
- 3. More was left for future use.
- 4. The yield of corn was higher.

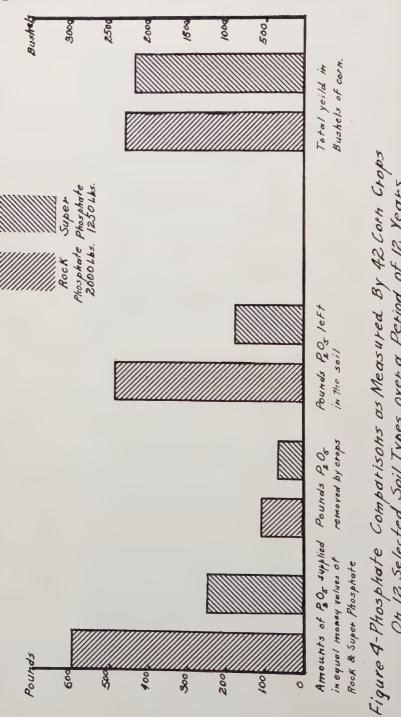
Of special interest is a unique study on the M-7 plots of the Agronomy south farm at Urbana. Here 1,500 pounds of rock phosphate were applied in 1935 and allowed to be residual for 15 years. At the same time in 1935 applications of superphosphate were begun at the rate of 100 pounds an acre a year. The super was continued until the same amount of money had been spent as for rock. This occurred in 1942, 8 years later, and then the super was allowed to be residual until the end of the 15-year





2000 lbs. per acre of Rock Phosphate

Figure 3.- M-14 Urbana 10 Year Average Rock Phosphate vs. Super Phosphate on Pasture Grasses & Legumes



OH 12 Selected Soil Types over a Petiod of 12 Years

period. Fig. 5 is a graph of the result trends. Rock phosphate returned a gross of \$129.67 or \$8.65 per dollar invested. Superphosphate grossed \$73.54 or \$4.90 per dollar invested. As this experiment progressed the crop showed need for potash. A new treatment was started in 1941 where 1,500 pounds of rock were applied in addition to potash. Fig. 6 shows the trend of the response to this treatment. In 9 years there was a gross return of \$83.17 or more than from a similarly treated plot with superphosphate over a period of 15 years.

#### RECENT DEVELOPMENTS

In recent years bulk storage and custom spreading have expanded so rapidly that one community may have four or five of these services. Rock phosphate lends itself especially well to this method of handling. In bulk storage of rock phosphate there is no corrosion, moisture absorption, or caking problems. The material remains in perfect condition until used. Custom spreading appeals to the user for several reasons. He saves the costs of bags and bagging, also labor and machinery for spreading. All this has made it easy to use. The yearly tonnage used figures

shown in Fig. 7 for the last decade are ample proof.

The most recent development is custom blending rock phosphate with whatever amounts of nitrogen, potash, or both, may be needed on a field as determined by soil tests and management history. This service is being offered by several progressive distributors at the present time. This type of service is spreading very rapidly. It has a great deal of merit and may easily enough revolutionize the program of the entire fertilizer industry. The companies give a soil testing service then supply either a basic or maintenance application of rock phosphate blended with the proper amount of N and K. To me this looks like the first attempt by industry to actually try to apply plant food to the soil according to the deficiencies in the soil and the needs of the crops. It has all the advantages of a materials program and a package program without the disadvantages of either.

Custom blending works this way. For example, a field not previously treated shows by tests need for 80 pounds of N, 1,500 pounds of rock phosphate, and 200 pounds of KCl an acre. Such an order comes into the plant and the materials are weighed out in correct proportion from separate bins moving into the spreading truck as a unit, taken to the field and all applied in one operation. In case of maintenance requirements the rock phosphate

may be cut to 400 or 500 pounds.

#### SUMMARY

History, records, and new developments have been given relative to the use of rock phosphate in Illinois. They justify our continuous effort and enthusiasm for its use.

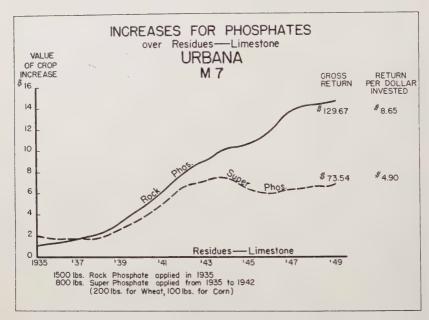


Figure 5.

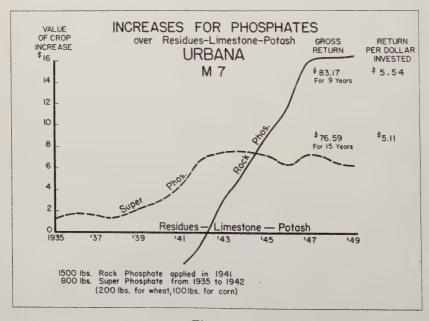


Figure 6.

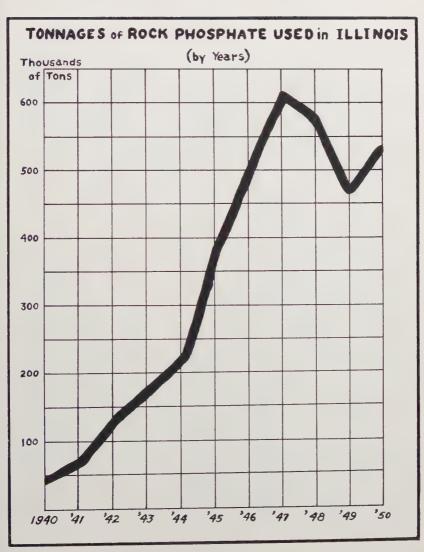


Figure 7.



Rock and superphosphate on unlimed soil, Raleigh soil experiment field, 1951.



Corn Yields Oblong Soil Experiment field, 1945.

(KN)

43 bu. Potassium, nitrogen

(RKN)

Crop residues legumes (KN) 56 bu.

(RLKN)

Limestone (RKN) 93 bu.

(RLPKN)

Rock phosphate (RLKN) 104 bu. Note: The Raleigh and Oblong fields

represent some of the poorly drained level prairie soils with impervious sub soil layers of Southern Illinois.



M-11 plots Agronomy South Farm, Urbana, 1947. (0)No phosphate 64 bu.

(RP)

Rock phosphate 88 bu. (O-20-O)

Superphosphate

79 bu.

Note: All plots have limestone, potash and nitrogen applied, 1600 pounds of rock phosphate was applied in 1946, 100 pounds of O-20-O is applied annually to each crop in the rotation of corn and soybeans. The photograph is of the 1947 yields. The yield figures are a four year average including 1950.

Figure 8.



Dr. W. L. Burlison, Head of the Department of Agronomy, University of Illinois, explaining the basic work of the Morrow Plots to a group of visitors, always closes with the dictum "This work must go on."

#### LITILIZATION OF PHOSPHORUS FROM VARIOUS SOURCES

#### W. L. Nelson\*

Superphosphate has been the standard source of phosphorus in commercial fertilizers with ordinary or single strength superphosphate being used much more than treble superphosphate in the Southeast. An important development in the commercial fertilizer field in recent years is ammoniation of superphosphate. This process favors the conversion of the monocalcium phosphate to the dicalcium and tricalcium forms. Rock phosphate and basic slag have been used for many years in certain areas. Lately, interest in other sources of phosphorus such as dicalcium phosphate, tricalcium or fused phosphate and calcium metaphosphates has increased.

The objective of this paper is to present information on source of phosphorus from the standpoint of efficiency of uptake of phosphorus by plants. Radioactive phosphorus has proven to be a valuable aid in such studies and much of the data reviewed will be based on work in which radioactive phosphorus was used as a tracer. Through such studies the efficiency of the various sources of phosphorus can be determined even without yield re-

sponses.

The utilization of certain sources of phosphorus will be discussed by crops.

#### COTTON

On a soil containing 67 pounds of  $P_2O_5$  (Truog) the percentage of phosphorus in the plant derived from dicalcium phosphate was distinctly lower than from the other sources (Figure 1) (4). On a soil containing 288 pounds of  $P_2O_5$  dicalcium phosphate again gave the lowest proportion of fertilizer phosphorus in the plant (Figure 2). On this soil alpha tricalcium was not so effective as the other three sources. Calcium metaphosphate was somewhat more effective than any of the other sources, however. In these experiments the fertilizer was placed in bands three inches to each side of the seed and two inches below. There were no significant differences in the yields of cotton obtained from the various sources.

#### CORN

On a soil high in phosphorus, 319 pounds of  $P_2O_5$  per acre, corn plants receiving phosphorus as superphosphate and as calcium metaphosphate were consistently higher in percentage of

<sup>\*—</sup>Director, Soil Testing Division, State Department of Agriculture and Professor of Agronomy, North Carolina State College of Agriculture, Raleigh.

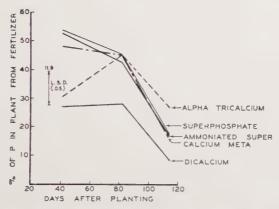


Figure 1.—Percentage of phosphorus in the plant derived from the fertilizer as influenced by the source of phosphorus for cotton on Norfolk sandy loam containing 67 pounds of P<sub>2</sub>O<sub>5</sub> per acre. (50 pounds of P<sub>2</sub>O<sub>5</sub> applied. The L.S.D. (.05) is for treatment means).

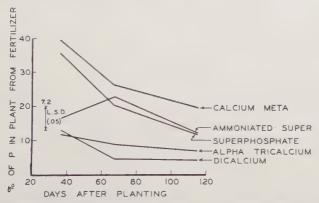


Figure 2.—Percentage of phosphorus in the plant derived from the fertilizer as influenced by the source of phosphorus for cotton on Norfolk sandy loam containing 288 pounds of  $P_2O_5$  per acre. (50 pounds of  $P_2O_5$  applied. The L.S.D. (.05) is for treatment means).

phosphorus derived from the fertilizer than those plants receiving alpha tricalcium phosphate (4). The percentage of phosphorus in the plant derived from each of the three fertilizer materials decreased consistently throughout the season. The fertilizer was placed in bands as described for cotton. There was no yield response to phosphorus on this soil.

#### SMALL GRAIN

In Iowa there was an interaction between the acidity of the soil and utilization of phophorus from the various sources (7). On a Clarion soil, pH 5.6, calcium metaphosphate was a less efficient source of phosphorus for oats than either dicalcium or

alpha tricalcium phosphate. However, on a Webster soil, pH 6.7, there was little difference among these sources. No source was better than superphosphate on either of these soils. The phosphorus was broadcast and disced in. There were no significant differences in yield.

In an experiment with wheat and barley in Colorado (6) superphosphate and calcium metaphosphate were much superior to dicalcium and tricalcium phosphates, with the two former sources giving increases in yield of wheat. This experiment was

conducted on a calcareous soil.

#### TOBACCO

Work in North Carolina showed that ammoniated superphosphate, when compared with ordinary superphosphate, produced a slight decrease in percentage of phosphorus in the tobacco plant from the fertilizer (8). Ammoniation of superphosphate reduces the amount of water soluble phosphorus (5) as a result of the reversion of part of the monocalcium phosphate to the more insoluble dicalcium and tricalcium phosphates.

#### SUGAR BEETS

Experiments on calcareous soils in Colorado showed that superphosphate and calcium metaphosphate gave a higher percentage of phosphorus in the sugar beet plant from the fertilizer than did dicalcium and tricalcium phosphates (6). At one location the two former sources produced significantly higher yields than did the two latter sources.

There was an interaction between placement and utilization of phosphorus from the various sources (6). Placement of the phosphorus in a single band 4 inches deep and 4 inches to the side was compared with phosphorus mixed with a rototiller in a band 4 inches wide and 4 inches deep. There was a greater uptake of phosphorus from superphosphates and calcium metaphosphate when these sources were placed in bands. On the other hand, with dicalcium phosphate, the rototiller placement gave the greatest uptake of phosphorus. The availability of dicalcium phosphate is apparently influenced by the root-fertilizer contact. With the more soluble sources rather complete mixing with the soil may favor greater reversion than is obtained with band placement, however.

#### **LEGUMES**

Superphosphate gave a higher percentage of phosphorus in Ladino clover from the fertilizer than did calcium metaphosphate, tricalcium or dicalcium phosphates (1). This experiment was conducted on a Mardin soil, pH 5.3. As with sugar beets,

there was an interaction between placement and the utilization of the sources. There was a greater uptake of fertilizer phosphorus from superphosphate and calcium metaphosphate drilled than with these sources broadcast. Placement did not affect the uptake of phosphorus from dicalcium or tricalcium phosphorus

phates, however.

Fried and MacKenzie compared superphosphate and rock phosphate on soils having a pH of 4.9, 5.5, and 5.8 respectively (3). The rock phosphate was added in amounts to give approximately four times as much P2O5 as supplied by the superphosphate. Alfalfa and vetch were grown. The percentage of phosphorus in the plant coming from the rock phosphate decreased rather markedly with decreasing acidity. This reduction was not as noticeable with superphosphate. On the most acid soil alfalfa absorbed a considerably higher percentage of phosphorus in the plant from the rock phosphate than from superphosphate. With legumes, as is true with other crops, if any treatment or source reduces the phosphorus in the plant to the critical level, the yield will be reduced. If a treatment or source does not reduce the phosphorus to a critical level, however, the relative ineffectiveness of the treatment or source is not significant as far as crop production is concerned.

A comparison of rock phosphate and superphosphate in a red clover, corn, and wheat rotation conducted for 20 years revealed it is necessary to apply somewhere between 3 to 7 times as much phosphate in rock in order to obtain a response equal to that obtained from superphosphate (9). Red clover was somewhat more efficient in utilizing the highest rate of rock phosphate

than was corn or wheat.

In Alabama, rock phosphate when used in amounts to give twice as much phosphorus as furnished by superphosphate was much less effective in increasing yields of winter legumes, corn and cotton than was superphosphate (2).

### SUMMARY

1. The efficiency of the various sources of phosphorus varies considerably.

2. This efficiency is affected by the acidity of the soil. The more insoluble sources are more available on the acid soils.

- 3. The efficiency is affected by placement. Band placement brings about increased uptake from the more soluble sources.
- 4. Crops vary in capacity to utilize the more insoluble sources.
- 5. Under the conditions in the Southeast, superphosphate is a satisfactory all-around source of phosphorus.

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### GENERAL COMMENTS ON PHOSPHATES

### VINCENT SAUCHELLI\*

Referring to Prof. Lang's eulogy of the C. G. Hopkins legacy on phosphate thinking at the Illinois Station, may I say that his presentation is by no means shared by many of his confreres on the research staff at that Institution. Hopkins was a remarkably strong character and in his day did a marvelously good job of getting farmers interested in sound practices. But a great deal has been learned since his time both here and abroad about the relative merits of different sources of phosphorus and the interrelationship in the soil between phosphorus and many of the other nutrients. Dr. E. E. DeTurk, Dr. R. H. Bray, and Dr. L. T. Kurtz, of the Illinois Station, have given much serious thought to these problems and have published their research which is at some variance with Prof. Lang's main thesis.

World agriculture, it seems to me, has given a definite answer regarding the relative merits of rock phosphate for direct application and superphosphate: during the last year about 20 million tons of superphosphates were consumed in world agriculture as against a total of about 800,000 tons of rock. That has been about the proportion for many years. In our own country Illinois has been the only state that has consumed rock phosphate for direct application in significant amounts. There must be a reason why farmers persist in preferring processed phosphates to the raw material. I suspect that reason has to do with profi-

table returns.

Now, to discuss briefly some other items bearing on phos-

phates.

Because of the close interrelationship among the several branches of agricultural science and the growing complexity in the relationship of all known plant nutrients, it is necessary for workers in this field to broaden their knowledge by going beyond their individual domain. All of us should at least have some acquaintance with the purpose and techniques of workers in other allied fields. The chemist and physicist have been able to help solve problems in the biological field, and the biologist in turn can contribute something to the others. Yesterday's program on methods emphasized this: even though it did make us all aware that ions, spectroscopes, amperes, voltages, photometers, aspergillus niger—the concepts and tools of the chemical, physical, and biological laboratories—can be used as a team, or group approach to solve a common problem. Last week in Baltimore at a symposium on copper at Johns Hopkins, the same thing was illustrated—representatives of the various branches of science

<sup>\*—</sup>Director, Agricultural Research, The Davidson Chemical Corporation, Baltimore, and Chairman, Fertilizer Industry Committee on Radioactive Research.

met to discuss the many interrelationships of this element to soils, plants, animals, and humans.

The importance of fundamental research as contrasted to applied research is being recognized by all major industries as a safeguard to their future. It has been my purpose on many opportune occasions to point out to scientific groups that the fertilizer industry is indeed interested in and fosters fundamental research. This has been revealed in diverse ways, but primarily by establishing fellowships at universities and institutions and by outright grants-in-aid with no strings attached, for the sole purpose of pushing back the frontiers of agricultural science.

One of these manifestations is represented by the creation and purposes of the Fertilizer Industry Committee on Radioactive Research, to which your Chairman alluded. This Committee was organized in the fall of 1946 and is still functioning, and represents a good cross section of the miners, processors, and mixers of the American fertilizer industry. It came into existence because some forward-looking men in the industry whose imagination had been excited by the atomic events of that period believed that this new power which burst so dramatically upon the world could and should be utilized in agricultural research. A generous fund was contributed to get a training program started as a joint project between the industry and several state and federal research agencies. The results of the first year's work attracted much attention, even though it was only a beginning. Men had to be trained in the new tracer technique, instruments had to be purchased. The able leadership of such men as Drs. Dean, Hendricks, and Parker, of the U.S.D.A., Bureau of Plant Industry, at Beltsville, enabled the project to get off to a good start. Dr. Nelson is one of the early workers on that program. From that initial effort the project has now grown to include this year about 20 agricultural experiment stations in this country and one in Canada. The tracer technique is being used extensively on all major soil types and cash crops to find out the most efficient methods of fertilizer placement and the relative advantages of different plant food sources and how plants utilize soil and fertilizer phosphorus. In most of these investigations radioactive phosphorus is used simply as a tracer. Remember, this technique supplements, not supplants, the other techniques of the chemical, physical, and biological sciences. This project represents a splendid cooperation between industry and governmental research agencies and shows what can be accomplished in the best interests of both parties by such joint efforts. May we have more similar programs in the future.

Problems involving soil phosphorus, the use of phosphatic fertilizers, and the phosphorus nutrition of plants are many and exceedingly complex. To begin with, the chemistry of the phosphoric acids itself is complicated; then we introduce phosphates into a wide range of soils differing in clay, humus, iron,

and aluminum, pH, and other factors. As if these problems were not enough, we multiply them by introducing living plants into the system, plants which differ widely as to phosphoric acid and other nutritional requirements. Is it to be wondered at that the field for more intensive research in this dynamic soil-nutrient-plant system continues to challenge all branches of agricultural science? Much has been accomplished; vastly more needs to be achieved. Atomic energy to solve many of these problems, is an ever present hope.

We are assembled here in this great state of Florida. It is only proper that I, representing one of the local phosphate rock miners, should call your attention to Florida's place in the phosphate world. The fertilizer industry is celebrating this year its 100th anniversary of the manufacture of mixed fertilizers. Starting in England, a little over a century ago—1843 to be specific the superphosphate industry was gradually expanded into a world-wide service industry producing upward of 20 million tons of the product a year. The fertilizer industry is founded on phosphates. Our own domestic superphosphate industry has facilities for producing at the rate of 14 to 15 million tons of normal superphosphate per year. The last year of record it produced about 11 million tons of 20% superphosphate or its equivalent. The great bulk of phosphate rock used in that production came from mines in this state. Since 1880 Florida has been the most important source of supply. The mining industry starting here as a manually operated, pick and shovel operation, has grown into one of high efficiency, utilizing modern power-operated facilities such as many of you saw in last night's tour. It does an amazing job to provide the American farmer with low cost phosphate.

It may be pertinent to review briefly some aspects of fertilizer phosphorus and soil problems of the country. Most of you are familiar with these. For example, the most phosphorus deficient area is in the Coastal Plain soils of the South Atlantic and Gulf Coasts, where the average content of  $P_2O_5$  in the virgin condition of the surface foot of soil was estimated at from 0.0 to 0.4 per cent. This average increases as we go to the north and west. Although total phophorus is not a good index of the phosphorus fertility situation, it gives us some idea of possible reserves. Phosphorus may exist in a soil as a primary mineral, as phosphorus absorbed on the clay surface, and as organic phosphorus. Of these, the absorbed or exchangeable form and the organic phosphorus are important for immediate use by plants.

Now, we know that Phosphorus is being removed by crops and particularly by erosion, and some is replenished by fertilizers, crop residues, and animal manures. We also know from certain surveys that apparently more phosphorus is being returned to the soils in the South Atlantic States than is removed by all

harvested crops. Florida is particularly high in this respect. At one time some folks seriously considered government action, I believe, to reduce the amounts of fertilizer phosphorus being applied. Fortunately that did not happen. These survey data have to be interpreted intelligently. Farmers apply it in heavy amounts because they find it pays. The use of phosphorus or any other plant nutrient is to be related to its money return rather than to the amount removed by crops. Field tests here and in other areas of the humid region show conclusively that it is profitable to put on several times as much phosphorus as is removed by cotton, potatoes, tobacco, and alfalfa, and other cash crops. And general averages do not mean much; we know that farmers do not all put back the phosphorus on their soils to the same degree, the amount varies from farm to farm and from county to

county.

Well, to refer again to the radioactive studies, the tracer technique is another tool with limitations like all similar techniques. The radioactive phosphorus does not remain radioactive very long. Its radioactivity may last, say 5 to 6 months at the most, enough for one season's study. It is of no value to determine residual effects of phosphorus fertilization. Other methods must be employed for this phase and we know that most, if not all, of the residual fertilizer phosphorus does remain available despite "fixation." Because of the highly developed phosphate mining and processing facilities in this country, the American farmer is assured a supply of phosphoric acid adequate to meet his constantly growing needs. And the American public can be thankful that this nutrient, so essential to his health, vigor, and well-being, is being made available in generous quantities at all times by the American phosphate and fertilizer industry. Florida may be the Sunshine State; it seems to me it should also be equally proud of and proclaim to the world its unique position as the Phosphate State.

# II. A REVIEW OF TRACE ELEMENT RELATIONSHIPS TO AGRICULTURE

# A. METHODS OF ANALYSIS

# CHEMICAL METHODS FOR DETERMINING TRACE ELEMENTS IN PLANTS AND SOILS

W. O. ROBINSON\*



MAJOR ROBINSON

The determination of the trace or minor elements in plants and soils, whether by spectrochemical or by chemical means calls for the utmost skill and patience. It is really an expert's job, to be most meticulously performed with simple and transparent honesty. Trustworthy determinations of such small quantities as a few parts per million, especially tenths of a part per million, which in the cases of iodine, cobalt, and molybdenum are significant, require a sound background of theoretical analytical chemistry and laboratory experience, with constant checking by independent methods when possible, and constant vigilance in testing for blanks, and purity of reagents and for contamination by sam-

pling, grinding, and even by constituents of the air before and during the analyses.

# Standard Samples

How is the chemist, or spectrographer for that matter, to know that his results are reliable? He can attempt to recover a known quantity added to a sample. But this is not always as

<sup>\*—</sup>Senior Chemist, Soils Division, Bur. Plant Industry, Soils and Agricultural Engineering, U. S. Department of Agriculture, Beltsville, Md. Note—A quite detailed statement by Mr. Robinson is to be found in the appendix of this volume, pp. 270-278, concerning "The Minor or Trace Elements in Soils, Plants and Animals" that was released in mimeographed form by his Bureau in the U. S. Department of Agriculture shortly before the Winter Haven meetings.—Ed.

simple as it seems and there are serious complications. Obviously the best way is to establish standard samples that have been analyzed by competent analysts and by different methods, if

available.

For many years the American Association of Official Agricultural Chemists has had a system of referee standard samples that were sent out to collaborating members, mainly to try out various proposed methods of analysis. As a result this Association has its Book of Methods published every five years. In this book the main emphasis is on fertilizers, food and drugs. Methods of analyses of plants and soils are not so well developed, especially for the trace elements.

I believe that standard samples of plants and soils, prepared especially for their contents of manganese, boron, copper, zinc, lead, molybdenum and such other trace elements that may develop, to be important to agriculture. It is important, of course, that the major element contents of such standard samples be known, and also that contamination by sampling, grinding, and storage be reduced to a minimum. Such standard samples, as authentic as the National Bureau of Standards samples of industrial products and materials, should be available to analytical chemists and those engaged in quantitative spectroscopy in the field of agronomy. To serve best, these standards should be international in character. The Soil Science Society of Florida might well take the leadership in this matter, as they have long recognized the desirability of such standards.

## Specific Methods

For the determination of copper, zinc and lead, most chemists prefer the dithizone method. This process is described in detail by Sandell (8), A.A.O.A.C. Book of Methods (6) and Holmes (4). It is our experience that the mechanical shaking device described by Holmes and Mullins (5) contributes a lot to the reproducibility and reliability of the method. The extreme sensitivity of this method imposes penalties. The sample is small and must be well mixed and finely ground. Constant vigilance is needed to guard against contaminations. It is not an easy method. Some have preferred to estimate zinc with the polarograph after separation from interfering elements by dithizone.

A concrete example of the importance of accuracy in analysis and of establishing standard sample may be illustrated by giving in detail the data on the occurrence of molybdenum in plants and

soils that have been accumulated.

It seems probable that the chromograph technique as described by Stevens and Lakin (9) for geochemical prospecting could be used for some of the trace elements. They have successfully used the chromograph in locating nickel and copper bearing formations by testing samples of the overlying soils and plants.

Nichols and Rogers (7) have compared the spectrographic, colorimetric and polarographic methods for determining molybdenum. Their conclusion was that the colorimetric thiocyanate method is preferable except when only very small quantities are available. They report very high molybdenum in a sample of para grass, 310 to 370 parts per million. Results for other vegetation range between 19 and 57 p.p.m. Since Nichols and Rogers published this work in 1944 the colorimetric method has been improved by the addition of very small quantities of solutions of ferric iron and potassium nitrate before the development of the color.

# Molybdenum in Soils

We have made molybdenum determinations in over 300 United States soil samples, mostly profile samples, and results range between 0.7 p.p.m. in Vernon fine sandy loam, Guthrie, Oklahoma, to 31.6 p.p.m. in DeKalb silt loam, Bloom, Virginia. This is by far the highest. There was only one area where the molybdenum was anywhere nearly as high and this is on an experimental plot of Cecil clay loam near Raleigh, North Carolina. Over ninety percent of the determinations of molybdenum made range between 1 and 4 p.p.m. This relatively constant quantity of molybdenum in United States soils examined would seem to point to some biological factor tending to keep the molybdenum content of soils up to a certain level.

The above relative constancy with regard to the molybdenum content does not seem to hold for soils in other parts of the world. Dr. H. C. Trumble, now with Food and Agriculture Organization recently sent in three soils from Nicaragua. He learned it had not been possible to grow legumes on soils Number 1 and 2. However, legumes could be grown on soil Number 3. He immediately suspected molybdenum deficiency in Soils 1 and 2. In these two soils there was only the merest trace of molybdenum, if any at all, but No. 3 had 2.4 p.p.m. In Somerset, England, the soils of the "teart" lands contain up to 100 p.p.m. Mo. One soil from Puerto Rico, the Nipe, contained 20 p.p.m. in the surface horizon with average quantities only in lower horizons. A similar concentration occurred in the surface of an Hawaiian soil. This condition, however, is not always the rule with tropical soils, as several profile samples from Australia and Belgian Congo show only average molybdenum and no concentration on the surface.

Didier Bertrand (3) has reported European soils, mainly French, relatively very high in molybdenum. Twenty soils ranged from 4.3 to 69.0 p.p.m. Mo. Many of these soils are on Agricultural Institution grounds. Half of these soils are over 20 p.p.m. and the average is 27.8 p.p.m. Mo. This is over ten times the average of soils in the United States.

### Molybdenum in Plants

In the analysis of 50 different kinds of crop plants and common weeds (216 samples) on 25 soil locations in Maryland, West Virginia, Indiana and Virginia it was found that there was not a great difference in the molybdenum content of different kinds of plants, though, in general, smart weed and lambs quarters tended to be highest. The extreme ranges are from 0.1 p.p.m. Mo. in lespedeza to 8.8 p.p.m. for red clover on Miami soil in Indiana. The average for 12 samples of red clover was 1.85 p.p.m. Eight samples of smart weed averaged 2.90 p.p.m. All results are based on the dry weight and are for the entire plant above ground. All plants were collected during mid-August. There was not a good correlation between total molybdenum in soil and plant, though there is a distinct tendency for soils high in molybdenum to produce plants higher in that element. The dependence of the uptake of molybdenum by the plant on the reaction of the soil was somewhat better but there were small exceptions. In this, as well as in other studies, legumes were not higher in molybdenum than non-legumes on the same soil except on one site. In many cases non-legumes exceeded the legumes.

The average molybdenum content of 105 samples of alfalfa was 2.70 p.p.m. molybdenum with a range of from 0.1 to 9.4 p.p.m. These samples were from 10 states, and included 20 samples from the Yuma, Arizona, area which were all comparatively high. In this area the soil is comparatively low in total molybdenum. The molybdenum in the plant apparently comes from the irrigation water. Alfalfa from the eastern states is generally much lower in molybdenum than that from western states, but there are exceptions. On a heavily limed plot of Cecil clay near Raleigh, North Carolina, alfalfa had between 7 and 8 p.p.m.

O. A. Beath (1) reports a woody aster plant from the Morrison Formation in Utah which contained 333 p.p.m. molybdenum. Other samples of woody aster from this same formation contain 100 p.p.m. and over. We have analyzed pea seeds from the province of Boyaca, Columbia, S.A. with 91 p.p.m. Mo.

Pasture vegetation on the teart lands of Somerset, England,

is reported to contain as high as 100 p.p.m. molybdenum.

Beath, Draize and Gilbert (2) in 1934 were first to point out the toxic action of molybdenum in vegetation on cattle. They also called attention to the effect of molybdenum on bone malformation.

## Trace Elements in the Air

In confining methods of analysis to soils and plants we have overlooked the main environment of the plant from which the plant obtains by far the most of its substances. This main environment of plants is the atmosphere. From this the plant must obtain practically all of its carbon. Carbon, by the way, is

just about a trace element in the atmosphere.

There are but 3.5 parts of CO<sub>2</sub> in 10,000 parts of atmosphere or 128 parts per million carbon in the atmosphere. In the vicinity of industrial plants burning coal, the proportion of CO<sub>2</sub> in the air is only slightly increased, as analyses have shown. The tremendous capacity of plants, large bodies of water, particularly the ocean to absorb this CO<sub>2</sub> tends to keep the CO<sub>2</sub> in the air at a constant level. But how about other trace constituents? There are large quantities of methane, volatile sulphur compounds, etc. being continually given off as marsh gas from decaying organic matter. The numerous bubbles arising from submerged organic matter in sluggish streams and ponds is a familiar example to all. This marsh gas consists of carbon dioxide, air, methane, and even hydrogen and carbon monoxide. One may even question if rather volatile and stable organic compounds of the trace elements are not present in some small quantity.

The analytical methods for trace elements in the atmosphere have not been developed. Following damages by smelter fumes and chemical manufacturing some recording devices have been made but they are adopted for relatively high concentrations only. For sometime I have been interested in a device which should give, with some accuracy, very low concentrations of the trace elements in the atmosphere. If a liter vessel built to withstand 1500 lbs. per square inch, were connected with a compressing pump, so that the air could be quantitatively compressed to 1500 lbs. per square inch we would have from 12 to 14 grams of air compressed into the vessel. In most of the humid east the air is over half saturated with water vapor so that, when the pressure inside the vessel reaches 2 atmospheres, minute water droplets form, and in condensing on nuclei, carry down the impurities contained in the air. If the operation is continued to 10 atmospheres there might be formed as much as 0.3 m.l. of water.

The contents of the vessel could then be frozen, and the gases led through a system of impinging plates, and suitable absorption tubes for the desired trace elements or compounds. Ten such fillings would represent roughly 120 grams of air, and might yield as much as 3 m.l. water suitable for the determination of a number of elements by the spectrographer or for sulfur, fluorine and chlorine, etc. by chemical means. No doubt the water condensed by concentration in the first chamber of the compressors of liquid air manufacturers would yield many valuable clues to the presence of trace elements in the atmosphere.

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# THE USE OF SPECTROGRAPHIC METHODS IN THE ANALYSIS OF SOILS AND OF PLANT AND ANIMAL TISSUES IN TRACE ELEMENT STUDIES

### T. C. ERWIN\*

The adaptability of certain physical and chemical methods for determining the trace element content of various agricultural materials was discussed in brief detail by Rogers and Hughes (1) at the time of the first symposium on this subject on the forum of this Society in Gainesville in 1940.

In this review particular emphasis was placed on the usefulness of dithizone extraction methods which were under study at that time and on the adaptability of the spectrograph, especially for exploratory studies in the broad field of trace element relationships to agriculture. The semi-quantitative and the precision procedures as developed at that time for the spectrograph were reviewed. In the meantime both approaches have been considerably improved not only by a more extensive medication of the sample but also by the availability of a much more versatile and accurate microphotometer.

## Sample Preparation, Including Pelleting

The definite experience of certain trace element losses during sample preparation both by the wet combustion procedure and by ashing in the usual manner at "controlled" temperatures greatly accentuated our interest in the pelleting of the sample so that it could be placed in its entirety in the arc and burned during the period of normal plate exposure. The above studies included the spectroanalysis of captured smoke samples which showed definite losses of some of the trace elements varying with the type of plant materials studied and the contained elements.

These pellets (1/4) were made with a press capable of delivering 80,000 pounds per square inch. Under such a pressure no cementing substance was necessary for any of the materials that it was found desirable to study. For arcing, the pellets were placed in 5/16" cavities formed by a special tool in the carbon electrode.

Some interesting results were obtained and some very definite advantages are thought to be available through the pelleting procedure though a considerable amount of work remains to be

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<sup>(1)</sup> Rogers, L. H. and Hughes, R. C., Proc. Vol. II, Soil Science Society of Florida, pp. 59-67, 1940.

done with it before it can be regarded as fully routine. The principal trials were made as a rough quantitative procedure by running samples of known levels of the unknown elements under a set of standard conditions as to pellet size and exposure characteristics and then plotting line density and quantity of element curves before running the unknown sample and comparing it with the standard curve. Some of the advantages are, of course, speed thru the avoidance of the tedious ashing procedure and its accompanying dangers of contamination and losses.

While the pelleting procedure is subject to numerous possible errors it was found quite satisfactory, for instance, in roughly determining the molybdenum content of forage samples. Doubtless the greatest source of error is the lack of homogeneity in the plant sample under study as only 1/10 gram of sample was taken for the purpose and this could not be ground or homogenized in any way without quite special equipment. Thus one of the most difficult problems in connection with the pelleting procedure is the preparation of the sample itself, especially in the case of plant parts, in order to insure that a truly representative portion is taken for the small amount that can be included in the pellet.

In the meantime all samples that have been ashed for spectroanalysis have been processed at the lowest possible heat. However, as intimated above, in order to burn to an acceptable ash, samples must ignite at some time or other and they are then exposed to an uncontrolled temperature even though it may be only for a comparatively brief period.

### ROUGH ESTIMATE PROCEDURE

In the rough estimate procedure weighed amounts of the ashed soil, plant or animal materials are burned in the arc in juxta positions on the plate against the spectrum of a synthetic standard containing varying amounts of 30 to 40 elements of potential interest that are detectable on the plate under the conditions of test. In the case of plant materials the base is largely made up of sodium, potassium, calcium, magnesium and phosphate while in the instance of most mineral soils in Florida it is largely silica, depending considerably upon soil type. Of a group of some 34 trace elements so listed for routine examination of plates the limit of detection of 26 of them was placed at 1, 2 at 4, 1 (zinc) at 6 on the large Littrow Spectrograph and at 1 on the Zeiss, 2 at 7, 2 at 8 and 1 at 10.

Thus, by running 2 plates with a proper control, reference estimates can be had on 30 elements or more with the sensitivity varying, of course, for each element. The major elements calcium, sodium, magnesium and potassium can be read as low as 1 p.p.m. whereas the sensitivity of phosphorus is very poor. The operation of this method is shown quite clearly in certain papers

of the Symposium referred to above (2) where many trace element values are reported on soils as well as plant materials.

As the term indicates, the rough estimate procedure lends itself especially well to exploratory or survey types of study. This of course makes it especially useful in such a field as agriculture that involves so many different though closely related materials (soils, fertilizers, plant and animal tissues) and particularly on account of the many complex biological factors that may be involved at different times. Discoveries by this method that have had a tremendous influence on Florida agriculture which might be mentioned must always include cobalt and molybdenum, as well as zinc. The former was first detected by this means as the beneficial element in a particular source of pyrites in New Zealand capable of curing what was known over there as "Bush Sickness," the apparent equivalent of one of our most severe forms of "Salt Sick" in Florida. Likewise molybdenum, an element now to be reckoned with where excesses are to be found in the herbage as, for instance, on some of our organic soils, was first observed in Dallis grass from the Everglades Station with the use of the spectrograph. Again, it was through the use of the spectrograph that zinc was first established as the deficient element in the well known "Frenching" of citrus that has caused very heavy losses to this industry in the past. In this instance it was the small Zeiss unit that was used since it was found to be much more sensitive to this element at the time of these studies than was the large Littrow.

## QUANTITATIVE PROCEDURE

This procedure consists largely of adding a known quantity of an internal standard to a known quantity of homogenized ash of the unknown. This standard can be any element not found in the sample in appreciable quantity but should be so selected that its excitation characteristics match those of the unknown element(s) as closely as possible. Elements in common use for this purpose are palladium, tellurium and tin.

After thoroughly mixing with the standard, a non-specific quantity of the mixture is burned in the arc in such manner as to give specific lines of reasonable density. The intensity ratios of the unknown to the standard element are then determined by the process of determining line density with the microphotometer and then calculating the correction by plate calibration for back-

ground density.

The accuracy of the method is dependent largely on the selection of an internal standard the various characteristics of which match those of the unknown as closely as possible. With

<sup>(2)</sup> Symposium—The "Trace" or "Micro" Elements in the Service of Florida Agriculture. Proc. Vol. II, Soil Science Society of Florida, pp. 51-115, 1940.

a properly selected pair the method should be reproductible within an error of 5 percent. However, in the interest of speed in the face of large numbers of samples to be studied, and in the need for multiple determinations, the method has been expanded to compare as many as six unknowns with one internal standard. Certain errors developed in setting up this procedure but these were determined largely to be due to definite variations in the excitation temperatures of the standard element and the unknown.

In consequence of these trials it was determined that for all practical purposes most of the elements of interest in this field could be placed in one of three groups where any element in the same group would serve as a suitable standard for any other of the group. These groups were formed by establishing the amount of excitation that developed in individual elements at various times during the arcing. Thus, one group, well represented by copper and tin, burns early since only a comparatively low temperature is required for their excitation. A second group, instanced by calcium, has a rather constant degree of excitation during the entire period of burn. A third group, e.g. aluminum and beryllium, requires the highest temperature and its members are, therefore, the last to appear on the plate.

It has been found that to develop the highest degree of accuracy, advantage must be taken of the use of double (e.g. copper and tin or iron and palladium) and even of triple standards. In this case particular care must be used in the selection of the standards to get them from the same excitation group since we now know that failure to match in this respect can prove the greatest source of error. In addition to the above and in order to attain greatest accuracy the lines of the unknown and of the internal standard should be of approximately the same wave length and the plate calibration curve must be run at that wave length. Therefore a series of plate calibrations will be necessary for best accuracy in different regions of the spectrum. With good care in the handling of all these limitations, errors as low as 5 percent should be attainable.

#### SUMMARY

The principal trace elements of interest to Florida Agriculture and to which most attention is being given at the present time are seven in number, namely copper, manganese, cobalt, zinc, iron, boron and molybdenum.

The place of the spectrograph in any comprehensive study of these and other trace elements in such a complex biological field has been well established though the methodology of the approach is constantly in need of improvement.

While the outstanding individual findings to date in this field in Florida thru the use of the spectrographic technic have been cobalt in relation to "Salt Sick," molybdenum in certain muck grown forages in relation to scouring of cattle and the consequent need for extra medication with copper, and the deficiency of zinc in relation to citrus "Frenching" under certain conditions, it also has helped tremendously in the study of certain interrelationships of these elements in the animal body such as that of cobalt intake in the steer to a much more favorable storage of copper in the liver of the animal under otherwise identical conditions. Its extensive use in the routine analysis of soil, plant and animal samples also has helped immensely in the handling of many problems and it doubtless will be of even greater assistance in the future if requisite time and effort are given to the improvement of the methods presently in use.

# POLAROGRAPHIC ANALYSIS FOR MINOR-ELEMENTS IN PLANTS

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Applications of minor-elements to correct abnormalities in plants were studied as early as 1927 in North Carolina by L. G. Willis (7). Despite these early beginnings, there is little definite information as to the frequency of occurance of minor-element deficiencies and the soil types involved. The use of plot tests for locating sites where crops respond to applications is obviously tedious and expensive. Surveys by foliar analysis seem likely to be more efficient in finding deficiency areas. A survey of this kind was carried out in 1948 in connection with studies of the mineral nutrition of strawberries. Leaf samples were collected from 300 commercial fields for determination of copper, zinc, manganese, and magnesium. The analytical procedure developed for this work included the use of the polarograph for copper and zinc. Aspects of these determinations will be discussed here.

Leeds and Northrup Company (2) have just released a bibliography of polarographic literature, containing 2208 references. Relatively few are concerned with the analysis of biological materials. Thus, of seventy-five on copper, only nineteen are for biological samples. For zinc, fifteen of ninety-one articles are concerned with biological materials. For manganese, there are two; for cobalt, two; for molybdenum, one; and for boron, none.

In the United States, microgram quantities of copper have in most instances been determined by colorimetric methods, the most popular of which have utilized "dithizone" or sodium diethyldithiocarbamate as color-forming reagents. Many procedures have employed dithizone for segregating the trace-elements before measurement by other means. Reed and Cummings (5) however, for a polarographic method, removed interfering iron and aluminum by precipitation with an excess of ammonium hydroxide. The filtrate containing copper was evaporated to dryness and the residue dissolved in a supporting electrolyte of acid sodium citrate for obtaining polarograms. In a similar procedure for zinc by the same authors (4) the iron and aluminum were precipitated by adjusting the solution of plant ash to pH values between 4 and 5. The filtrate was evaporated to dryness and the residue dissolved in a supporting solution of ammonium acetate and potassium thiocyanate for making polarograms. These precipitation methods of separation, despite their simplicity, have evidently not been used widely by other workers, probably because of the opportunities for losses by absorption on the precipitates, and contamination from the filter paper.

Typical methods employing dithizone to isolate zinc for determination by the polarograph are those of Takazawa and Sherman (8) and of Walkley (6). Holmes (1) published a method

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for the determination of zinc, cobalt, copper, and lead in soils using dithizone. Copper was extracted at pH 2.5 (thymol blue) and zinc was then extracted from the same solution after the pH value was adjusted to 8.3 (thymol blue). Both zinc and copper were measured by means of the colored dithizone complexes.

For the strawberry foliar analysis survey mentioned earlier a procedure was sought which would permit the determination of both copper and zinc in aliquots of the same sample. Holmes method seemed promising for isolation of the two elements, but was found unsuccessful due to the fact that about one-third of the zinc in the sample was extracted with the copper at pH 2.5, giving low values for zinc from the subsequent extraction at pH 8.3. This difficulty was surmounted by extracting both zinc and copper together at pH 8.3, diluting to known volume, and using separate aliquots of the extract for copper and zinc, respectively. It would be advantageous to determine both zinc and copper polarographically in the same solution, but no supporting electrolyte has been found which permits the determination of both metals in the same solution at the low concentration levels found in plant samples. The convenience afforded by such a solution to support polarograms of copper at 2 to 8 micrograms and of zinc at 7 to 30 micrograms per milliliter would justify the expenditure of considerable time and effort directed toward its

Reed and Cummings (5) observed that copper was lost from plant tissue samples during dry ashing, and recommended that perchloric acid digestion be used instead, no losses being occas-

sioned by this procedure.

In the light of the foregoing considerations, the following procedure was developed and found satisfactory for foliar analysis of strawberry, the results of which have served to locate fields which were later shown to be definitely deficient in copper.

The fresh leaves were rinsed free of adhering soil by means of water redistilled from a Pyrex glass still, with light scrubbing of the leaf between finger and thumb where necessary, followed by rapid rinsing in two changes of re-distilled water. The excess moisture was shaken off and the leaf blades dried in an oven with forced circulation at 80 degrees centigrade. The dried leaves were ground in a small Wiley mill having no brass or bronze parts.

Two-gram portions of the sample were weighed into 50 ml. Kjeldahl flasks fitted with ground glass stoppers and having calibration at 50 ml. Two ml. of conc. nitric acid was added to each flask, which was then placed in a beaker on a warm hot-plate. When reaction had slowed somewhat, 2 ml. more of nitric acid was added and the heating continued. A third 2 ml. portion of nitric acid was added followed immediately by 2 ml. of 60% perchloric acid. The temperature of the hot-plate was gradually increased until oxidation of the organic matter was complete, leaving a colorless solution. Occasionally the digest would char somewhat, near the end of the digestion. The addition of two drops of con-

centrated nitric acid served to discharge the brown color. In some cases this color reappeared and was discharged by further 2-drop portions of nitric acid until finally the digest became perm-

anently colorless.

To the cooled digest in the flask was added 10 ml. of water, which was then boiled for a few seconds by heating over a gas flame (with agitation to prevent bumping) to expel free chlorine and to dissolve the salts present. After cooling, the solution was diluted to 50 ml. and 40 ml. aliquots transferred to a 200 ml. separatory funnel. The remaining ten ml. was used for determination of manganese and magnesium. To the solution in the funnel was added 3 ml. of 50% ammonium citrate and five drops of 0.05% thymol blue. Ammonium hydroxide was added until the red solution changed through yellow to blue. Five ml. of 0.2% dithizone in carbon tetrachloride were added and the funnel stoppered and shaken vigorously for one minute. The funnel was then allowed to stand until the solutions separated (five minutes) and the carbon tetrachloride layer was drawn off into a 25 ml. volumetric flask. The extraction was repeated with two more 5 ml. portions of dithizone solution, and the three extracts were collected in the same flask and diluted to 25 ml. with carbon tetrachloride.

A 10 ml. aliquot was withdrawn and transferred to a 20 ml. pyrex beaker for the determination of zinc. The carbon tetrachloride was evaporated by gentle heating on the hot-plate. To the dry residue in the beaker was added 0.5 ml. conc. nitric acid, 0.5 ml. 60% perchloric acid, and two drops conc. sulfuric acid. The temperature of the hot-plate was gradually raised until only the sulfuric acid remained in a fuming state. The beaker was transferred to a muffle furnace at 400 degrees centigrade for five minutes to expel the remaining sulfuric acid. At this point zinc and copper sulfates remained as a faint white residue in the bottom of the beaker. The latter was cooled and exactly one ml. of supporting electrolyte (6) (0.1 N NH<sub>4</sub>Cl, 0.02 N KCNS and 0.0002% methyl red) was pipetted into it, bringing the solution in contact with the sides of the beaker. After standing for 3 to 5 minutes, the solution was poured into an electrolysis vessel and the latter was connected to the polarograph. Pure nitrogen gas was bubbled through the solution for 3 minutes. The polarographic current-voltage curve was then plotted for the range -0.75 volt to -1.4 volt. Known amounts of zinc sulfate (0 to 30 micrograms of zinc) were evaporated to dryness in 20 ml. beakers

micrograms of zinc) were evaporated to dryness in 20 ml. beakers and taken up in supporting solution for plotting polarographic curves to produce a calibration curve of wave height versus concentration of zinc. From this graph, the levels of zinc in the samples were then read. Subsequently, two or three standards (20 micrograms of zinc) were run with each lot of 12 samples, to check the validity of calibration.

Copper was determined in the remaining 15 ml. of dithizone extract by transferring it to a 20 ml. beaker and converting the

metals to sulfates exactly as for zinc above. The cooled beaker containing the sulfates then received 1 ml. of the supporting electrolyte of Reed and Cummings (5) (equal volumes of 0.5 M NaOH and 0.5 M citric acid plus 0.005 acid fuchsin). After 3 to 5 minutes of contact with the beaker, the solution was transferred into a polarographic cell, de-oxygenated with nitrogen gas for 3 minutes, and the current-voltage curve plotted for the voltage range 0 to -0.6 volt. Known amounts of copper sulfate evaporated to dryness in 20 ml. beakers served as standards for ascertaining wave heights and these were plotted against concentration of copper in the solutions electrolysed. From this graph, the quantities of copper in samples were read. As for zinc, two to three standards (5 micrograms Cu) were run with each lot of 12 samples.

The procedures described here have served to measure quantities of copper ranging from 2 to 8 micrograms and of zinc ranging from 5 to 25 micrograms from samples of plant material. Precision of these determinations was found to lie within 10% of the amount of the element being determined and commonly averaged about 5% for determinations carried out on the same

sample on different days.

Purification of reagents, where necessary was carried out by the methods described by Piper (3). Perchloric and sulfuric acids of C. P. grade were found to be sufficiently pure. Hydrocloric acid and ammonium hydroxide were redistilled from Pyrex. Ammonium citrate was extracted with dithizone. Carbon tetrachloride was re-distilled when test showed the presence of intolerable impurities in a given lot. Dithizone solutions were prepared according to Piper. Commercial nitrogen gas was used without purification. With these precautions, blank determinations commonly yielded about 0.3 microgram of copper and 1.0 microgram of zinc.

Sample values were always corrected for the quantities found

in the blanks which were run with each lot of 12 samples.

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# THE ADVANTAGES OF THE FLAME PHOTOMETER IN SOIL AND PLANT ANALYSIS

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Although the flame photometer, to a certain extent, is more limited in its application than the spectrograph, it is finding wide acceptance as an instrument for the determinations of sodium, potassium, calcium, magnesium and manganese in solutions containing these elements. With improved electronic circuits and better burners its use soon may be extended to include more of

the minor elements, such as copper.

In the soil testing laboratory the flame photometer will quickly pay for itself by the time saved in determinations of potassium. Analyses for this element by the cobaltinitrite precipitation methods require considerable time while the more rapid turbidimetric procedures are entirely unsatisfactory unless temperature and other conditions during manipulation are very rigidly controlled. Even these methods, especially the latter, lose their required accuracy at low levels which are usually encountered with samples of soils low or deficient in potassium. With a flame photometer a single operator may develop the skill and technique which will allow the determination of potassium on as many as 100 soil extracts per hour. Furthermore, the results usually are found to be reproducible even at very low levels of potassium.

Tests made on a Beckman flame photometer equipped with the original type, large, metal burner with chimney indicate some slight interferences in the excitation of one element by another, but not sufficient to introduce errors which might be objectionable in routine soil tests. Sodium may increase the reading of a 15 ppm. potassium standard approximately 6 percent at 25 ppm. of the element and as much as 20 percent at 90 ppm. Such high values for sodium are seldom found in soil samples under conditions usually encountered in South Florida. Calcium up to levels as high as 3000 ppm. showed no effect on the excitation of potassium with a standard containing 15 ppm. potassium. Magnesium up to 150 ppm. showed no effect on the same standard.

Sodium, potassium or magnesium at the highest levels usually found in soil extracts showed no effect on calcium determinations ranging from 0 to 1500 ppm. Sodium, potassium or calcium had no effect on magnesium readings. Preliminary tests with manganese indicate no pronounced effects due to the presence of sodium, potassium or calcium at the highest levels normally present

in soil extracts.

Considerable time in converting the readings to ppm. or pounds per acre in the sample may be saved by adjusting the slit width

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and sensitivity for each set of readings in such a way that two standards representing positions on the curve will read approximately on the predetermined standard curve. By following this procedure the sample readings may be converted to the desired values by reading directly from tables prepared from the original standard curve. These standard tables may be used indefinitely without recalibration. Such a procedure is well adapted to routine soil testing where speed may be a more important factor than quantitative accuracy.

The flame photometer is equally well adapted to extracts of fresh plant tissue and solutions of soil or plant ash. The same solution should be used for extraction of the tissue or dissolving of the ash samples as is used for the standard solutions. This also may be the same solution used for extracting soil samples, thus making the same standards applicable to all types of analy-

ses.

Flame photometry has contributed a great deal to the speed and accuracy of chemical analyses and no doubt will find wider fields of application as improvements are made in the design and operation of the equipment.

# A MICROBIOLOGICAL ASSAY FOR AVAILABLE BORON IN SOILS

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It is generally agreed that correlation of chemical soil tests and actual crop requirements leaves much to be desired. This appears to be particularly true for boron. A partial explanation in this instance is indicated by the fact that boron may not be absorbed by the soil colloid like copper or zinc ions. A very slight application of borax above that needed by plants causes injury (13). Recognizing this, Schuster and Stephenson (10) developed the sunflower-pot-culture test for boron deficiency in soils. Results from this test are satisfactory but the method is time consuming and expensive. Steinberg (11) suggested the use of fungi to determine the essentiality of minor elements because of the similar physical and biochemical relationships of these microorganisms to the higher plants. Mulder (8) demonstrated this possibility earlier with his Aspergillus niger test for available copper in his investigations on the "reclamation disease" problem in Holland.

From 1939 to the present date, the occurrence of boron deficiency has been observed, especially in the sandy soils of the

coastal plains.

Jones and Scarseth (4) observed that high lime soils required more boron than acid soils and that applications of lime limited the availability of boron to plants. Midgely and Dunklee (7) found that calcium, barium, magnesium, and sodium carbonates were equally effective in fixing borates in soils, which strongly suggested that reaction may be the controlling factor in boron fixation. These workers demonstrated that boron fixation in alkaline soils was of a temporary nature. Naftel (9) suggested that liming soils stimulated microbiological activity to the extent that available boron is depleted. Hanna and Purvis (3) substantiated this claim to some degree by showing a rapid rise in carbon dioxide evolution when either lime or boron was added to acid soils. They proposed the use of this phenomena as a biological test for boron, and found *Trichoderma viride* to be especially sensitive to these changes

Marked response to boron by various species of *Penicillium* was shown by Koffler et al. (6) while investigating the possible use of boron to increase penicillin yields and inhibit bacteria. *Penicillium chrysogenum*, Strain NRRL-1951-B25 was especially

sensitive to various boron levels.

The purpose of this investigation was to develop a micro-

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biological assay for available boron in soils. Studies on the practical application of the method are being continued.

### EXPERIMENTAL

# Selection of Soils and Determination of the Approximate Boron Content

Random samples of Lakeland fine sand were taken from various locations in Alachua County where the soil was known to be deficient in boron. The approximate boron content of four samples of this soil was adjusted by treating with sufficient borax to roughly simulate deficient, adequate, abundant, and toxic conditions. A final analysis of the soils was made by the mannitol-titration procedure (2) to establish an approximate boron rating for the different samples. The results are tabulated as follows:

TABLE 1.

	TE BORON RATING OF TD FINE SAND (CHE	
Sample	Rating	p.p.m. Boron
A B C D	Deficient Adequate Abundant Toxic	Trace 0.2 0.5 0.9

### METHODS OF PROCEDURE

A standard complete mold nutrient medium was selected that had been tested in actual practice. Barton-Wright's (1) modification of Stokes' medium was used, principally because it contained all factors that permit a rapid development of mycelium and little or no sporulation (12). These factors include organic acids and a high Zn content, in addition to sources of Na, Cl, Mg, and Ca not commonly found in other media.

The optimum growth range for both *Penicillium chrysogenum* and *Trichoderma viride* was established by plating out these molds at 0, 0.1, 0.25, 0.5, 1.0, 3.0, and 6.0 p.p.m. of boron, using Barton-Wright's medium plus 2% of washed agar. This procedure was repeated, using 10% CaCO<sub>3</sub> in the medium, which brought the reaction from pH 4 to pH 6. The latter step was instituted in order to note any changes in the response to boron because of the weaker acid condition.

The representative unknown sample of soil was depleted of boron by saturating an amount of dry soil with C. P. methanol (5). In the absence of water,  $H_3BO_3$  forms volatile esters with the alcohols. Fixed or slowly available amounts of boron were

not considered in this study, since the readily available and not the fixed or slowly available amounts of boron was the object of this investigation. This procedure was considered satisfactory

for all general purposes.

In order to prevent any major chemical changes in a standard medium, especially when subjected to the heat necessary for sterilization, only 1 gm. of soil to 10 ml. units of nutrient was used. The small amount of soil in proportion to the large amount of nutrient was further selected because it was desirous that the buffer capacity of the medium remain unchanged in case soils of high alkalinity were tested.

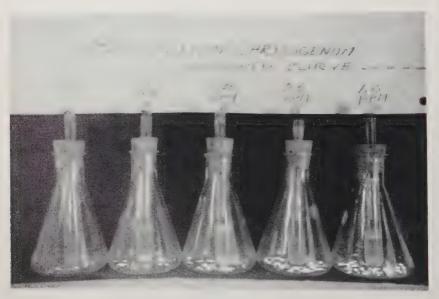


Figure 1.—Culture flask setup for absorbing CO<sub>2</sub> evolution in KOH solution during incubation.

For the final procedure, 250 ml. flasks were selected for the boron response series as well as for the duplicate unknown. The prescribed amounts of soil and nutrient were added and each flask marked as to its boron content. After autoclaving, inoculation, and incubation, the variation in the amount of mycelium produced by the different boron levels was considered to be proportional to the amount of CO<sub>2</sub> evolved (3). With this in mind, the CO<sub>2</sub> was measured by absorbing the gas in 10 ml. of 0.5 N KOH solution, which was conveniently added through a large tube (Fig. 1) at the mouth of the flask, prior to incubation. After a specified period of time, an excess of 2N BaCl<sub>2</sub> was added to each flask, and the free alkali titrated directly with 0.5 N HCl using thymol blue indicator. The entire procedure was performed without moving the test tube from the

flask. The mls. of standard acid needed to arrive at a definite yellow color was plotted directly on a graph to represent a growth curve. The results from the unknown sample were obtained in a similar manner and interpreted on the standard curve.

### RESULTS

All plates were incubated at 28 C. At the termination of 72 hours, only *Penicillium chrysogenum* exhibited any boron response in the acid series. For the Ca-treated series, both of the molds showed as much as 100% increase in growth and a definite response to boron. Within a few hours later, both molds quickly overgrew the plates, revealing that only the initial growth period appeared to be affected. The greatest variation to boron in the acid series occurred between 0 and 1 p.p.m.



Figure 2.—Growth curve based on titration values showing CO<sub>4</sub> evolution during period of incubation.

From 1 to 3 p.p.m., there was a slight variation and the actual inhibition at 6 p.p.m., indicating an optimum at about 3 p.p.m. of boron. For the CaCO, treated series, the same conditions occurred, except the optimum changed to near the 6 p.p.m. boron level. This appears to substantiate the claims of earlier workers. For the final results, it was decided to use *Penicillium Chrysogenum* in an acid medium with a range from 0 to 1 p.p.m. of boron.

A standard growth curve was made by using five 250 ml.

flasks containing 0, 0.1, 0.25, 0.5 and 1.0 p.p.m. of boron, respectively, and following the procedure described above. Inoculation was accomplished by adding one drop of a heavy spore suspension of *Penicillium chrysogenum* to each flask. After 72 hours, a definite visual difference was apparent in the number of colonies corresponding to the different amounts of boron present in the flasks. After titration, the standard growth curve was plotted (Fig. 2) and the duplicate unknown sample referred to this curve for determination of readily available boron.

The results obtained are presented in Table 2 for comparison by the chemical method.

Table 2

# COMPARISON OF BORON RATING OF FOUR SAMPLES OF LAKELAND FINE SAND BY BIOLOGICAL AND CHEMICAL METHODS.

Sample	Boron Rating	p.p.m. Boron	
	Doron Italia	Biological	Chemical
A	Deficient	Trace	Trace
В	Adequate	0.1	0.2
C	Abundant	0.2	0.5
D	Toxic	0.5	0.9

#### SUMMARY

A preliminary study of a microbial test for available boron in soils is reported. *Penicillium chrysogenum*, strain NRRL-1951-B25, appeared to be superior to *Trichoderma viride* in its

response to boron.

The addition of 10% CaCO<sub>3</sub> increased the growth of both molds as much as 100% and increased the optimum boron response from 3 to 6 p.p.m. The greatest variation appeared to be from 0 to 1 p.p.m. of boron; this occurred within a narrow range of 50 to 72 hours. Thereafter, the growth quickly equalized in all flasks. The medium changed from acid to alkaline conditions, probably due to the loss of carboxyl groups by excessive CO<sub>2</sub> evolution and the accumulation of the basic ions that do not enter to any extent into the structure of the tissue.

The investigation indicates that many soil fungi may be similar to higher plants in the variation and response to boron.

Penicillium chrysogenum was found to respond to various levels of boron under similar conditions of physical and chemical environment. This response was determined by the number of colonies present in the flask and by the amount of CO<sub>2</sub> evolved. This method appears to have merit as a microbiological assay for boron in soils.

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# B. TRACE ELEMENT RELATIONSHIPS TO THE HEALTH AND GROWTH OF PLANTS AND ANIMALS

# TRACE ELEMENT RELATIONSHIPS OF THE NORMAL GROWTH OF AGRICULTURAL PLANTS ON THE ORGANIC SOILS OF FLORIDA

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It is an interesting fact that at precisely the same time the first systematic studies of trace element relationships to plant growth on the organic soils of the Everglades were begun at the Everglades Experiment Station (Spring, 1927) the Brown Company of Portland, Maine and Berlin, N. H., made their first "test planting" of 1,000 acres of peanuts on identically the same type of soil on their extensive plantation, then known as Shawano, on the Hillsboro Canal about 12 miles below the Station, down in the heart of the Everglades. It was at this same time, too, that Mr. George E. Tedder, who had been Foreman of the Everglades Station since December 10, 1923, made the flat offer of \$5.00 per bean (\*\*) for every bean ever to be grown on "sawgrass land," so often had he seen planting after planting of all kinds of crops come up hopefully only to wither and perish without exception. Snap beans were of course understood.

Before briefly discussing the results of those early tests at the Experiment Station and the numerous others that have followed, it is regrettable to report that, due to the absence of treatment with copper in any form, not a single, mature peanut was developed on the entire 1,000 acres down at Shawano that had required many tons of seed for the planting. It is likewise regrettable that Mr. Tedder's earthly estate must needs find itself so wholly inadequate to meet the gigantic responsibility which he flung against it with such well-meaning abandon that Spring morning in 1927 in view of the developments that have followed. For if George were really to assume that responsibility and "Pay up," the National Debt quite readily could be wiped out with a single Postal Order from Belle Glade and, additionally, without cutting into the main body of the accumulated and accumulating revenues too greatly, enough moneys set aside to refurbish the whole earth against the enormous physical damage done by the most recent world war. In other words the good peat soil of the Everglades has produced many a bean since that time and is still producing them by the tens of thousands of hampers each year, due first to copper and second to manganese, insofar as the trace element relationships that have been developed are concerned. Zinc and boron have shown almost equal

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<sup>\*\*—</sup>In the presence of Mr. J. H. Hunter, Asst. Agronomist at that time, and the writer, then Soil Specialist.

indispensability for other crops under certain conditions so that these four elements have indeed proven themselves the "Four Horsemen" of Everglades agriculture, the developing need for phosphate and potash with the progress of cultivation and crop-

ping out of the soil being taken for granted, of course.

The initial set of trace element treatments referred to above involved a dozen chemicals and other materials including copper, manganese, and zinc, all in the sulfate form at different rates per acre. These treated plots were laid out in duplicate on freshly-cleared, very raw, sawgrass peat as long, narrow areas in such a way that a wide variety of agricultural plants could be planted across all of them as continuous rows interrupted only by narrow alleys running lengthwise between the plots. The nature of the sawgrass cover in those early days is well shown in Figure 1.

### THE PRIMARY PLANT RESPONSE

Inasmuch as these first plant responses to copper, manganese and zinc were outlined in some detail in Bulletin 190 (1927) of the Florida Experiment Station and have been referred to quite frequently since that time they now will be passed over quickly, the response taken for granted, as it were. However, since the above bulletin has been out of print for many years, a few of the photographs on a small scale will be included at this time especially to show the wide range of agricultural plants definitely requiring these trace elements for normal growth under the native conditions that prevail in this organic soil which is now officially known as Everglades peat. Particular reference is, of course, to copper in the raw, unburned, peat. The photographs of Figs. 2-8 with their brief legends appended really tell the story much better than words regarding these responses of all field and truck crops to these elements.

An unusual copper deficiency pattern is shown in Fig. 9 on the leaves of the sugar cane variety Coimbatore (Co.) 281. This frequently was mistaken for mosaic in the early days when the occurrence of such deficiencies in this and other farm crops of the area were the rule, rather than the exception, as at present.

Unusual responses likewise were obtained in those early days from a number of different materials. Mention already has been made of compost. Caustic lime also should be included. Then too, there was observed an extremely interesting plant response to treatment of the raw soil with creosote. The reaction of sugar cane to this material is shown in Figures 10 and 11. Further interesting observations as to the nature of these essential growth factors were made by layering canes from parent stools, where the soil had been well treated with copper and other necessary elements, down into raw soil that had received no treatment whatsoever. The extraordinary response to such a continuing contact with the parent stool is shown under greenhouse conditions in Figure 12 and under field conditions a little later in Figures 13 and 14.

The same type of complete responses also were obtained thru the use of copper on tree crops, as are well shown in those appearing in Figures 15-18.

### MANGANESE

While copper in one form or another has proven completely indispensable, even though it be present only as traces in compost or other crude chemical compounds, it was soon found that where the soil pH is near or above neutral (7.0) manganese becomes unavailable for a wide variety of plants as shown in Figures 19-22. When this condition occurs response is obtained by several means but notably by soil treatments with manganese or with sulfur or by dusting or spraying the element directly on-

to the foliage of the plant in one form or another.

Here again tree crops, such as palms, suffer the same as smaller plants when the availability of manganese becomes too much depressed by excessive lime in the soil. The four Figures 23-26 showing several different varieties of palm trees in the Palm Beach area are illustrative of this condition. These were some of the first treatments with manganese in this area. While these trees were on highly calcareous mineral soils, the response of these palms on high-lime organic soils is essentially the same. All survived as a result of manganese treatment in some form although all were near death at the time of treatment. These early studies have been followed up very energetically through the years, first, by Mr. John R. Wilson, and later by others, with excellent success on a commercial scale. It was at about this same time that the first response of citrus to manganese was obtained on a high lime section of the "Home Grove" of Mr. Walsh at Davie, where in his ridging operation he had practically capped his planting ridge with marl brought up from beneath the comparatively shallow layer of peat at the south end of his planting. These results were reviewed at the 1931 meeting of the State Horticultural Society and published in the Proceedings of the Society for that year.

### COMBINATION TREATMENTS

As might be expected, where a particular soil environment contains deficiencies of more than one element, nothing like normal growth in a plant requiring both could be expected from the use of either alone. This relationship became very obvious in the very first trials referred to above where the peanut plant was involved and under conditions of copper application to the soil (30 pounds per acre of bluestone in the row) immediately prior to the planting of the seed. The seeds on all treatments germinated promptly and came up uniformly but stopped growing on all plots after ten or twelve days, including those on the copper treatment. They then assumed either a low dense rosetted

form in the top with leaves yollowing and spotted, as shown in Figure 27, or grew up a few inches in tiny spindling plants. This was not true of the plants on the zinc treatment since they continued growth right on thru this early period but it was of a more erect, spindling type though they never grow to more than 6 to 8 inches in height. This delay in the early copper response and prominent activity of the zinc response thru the early period of growth naturally raised the question of prospective benefit from a combination treatment. It was largely on account of this strikingly differential response that the first, more detailed study to follow the very first treatments was with peanuts on fair sized plots with individual and all possible combination treatments of copper, manganese, zinc, caustic lime and stable manure, all five materials having given various degrees of response on different plants when used individually in the first tests.

Reference will be made in these studies only to the copperzinc response since it was so outstanding and so well demonstrated the point under test and discussion. Again, the plants on the copper treated plots came up to a good stand and, for the first five or six weeks looked very much like the plants on the untreated (check) plots. On the other hand, each of the uncoppered plots that received zinc again exhibited the same continuity of early growth observed before, but only of a spindling, abnormal type that eventually came to naught. In the instance of the combined treatment with copper and zinc, however, there was no delay whatsoever in the normal growth of every peanut plant on each plot receiving simultaneous treatment with both elements. Regardless of whatever other components any of the treatments contained, the copper-zinc combination was outstanding in the promptness, continuity and completeness of its response as is evident in Figure 28 where the plants from the dual treatment matured 5-6 weeks ahead of those receiving only the copper treatment. This response was well emphasized by the yield data which grew out of these plots. While no yield whatsoever was obtained from uncoppered plots, good yields and an early harvest came from the plots receiving the copperzinc combination and a good yield but delayed harvest from those receiving only copper sulfate. A closeup view of some of these plots is shown in Figure 29 while Figure 30 shows, above, a general view of the experimental setup before the storm of September 1928, and, below about a fortnight following it.

These reactions were discussed before the Plant Physiology Section of the American Association for the Advancement of Science in December, 1928 in New York but the paper was not

published at that time.

In subsequent studies on these same plots, after converting to general fertility work due to scattering of trace element treatments by the storm, and including adequate amounts of phosphorus and potash, along with supplemental trace element treatments, yields up to 3000 pounds of peanuts (Little Spanish) per acre were obtained along with the same amount of tops as hay. In these later studies the rapid cropping out of first potash and then phosphate was clearly demonstrated. In fact responses to either of these two major elements became almost as dramatic as those to copper or any of the trace elements that are reviewed above when the element was restored after the soil had been cropped to a very low level. The helplessness of copper in the absence of adequate supplies of the major elements is well shown in the results of some of the early greenhouse studies presented in Figure 31.

Insofar as greenhouse work with the trace elements is concerned, much better results were obtained when improved sources of distilled water were to be had. This is understandable when it was found in the course of later work that passing ordinary tapwater thru a conventional still increased its copper content ten times. Redistilling thru quartz or passage thru absorbing resins have given good protection in work of this type as exemplified by the excellent results reported by Dr. W. T. Forsee, Jr., in Volume II, Soil Science Society of Florida and elsewhere.

### RESIDUAL VALUES IN THE SOIL

One of the earliest checks following the first cropping of the individual application of copper in the first series of treatments was on the localization of that 30 pound treatment that had been placed in the row and of the residual values that remained. This was first done with the common beggarweed by opening up the original line of planting with a small hand plow after first preparing light planting furrows between the rows, the plow being carefully cleaned between each such operation in any event. Both sets of rows were simultaneously seeded to beggarweed with the results that are shown in Figures 32 and 33.

It was obvious from the plant response that there was suficient copper remaining from the earlier treatment to adequately supply the additional planting since the plants made just as luxuriant growth as before. However, those plants between the rows and out of immediate contact with the residual copper failed completely even though they were in a soil filled with healthy, vigorous roots of plants growing 18 inches away but with a local contact with the copper already in the soil as residual from the earlier treatment. This tremendous permeation of the soil by plant roots is well shown by the block of rape roots excavated from the row to half way across the middle to the next one. This is shown in Fig. 34.

Naturally where response of plant growth is so unusual to such small amounts of chemical, great care must be taken in all field operations to avoid contamination. That is why the great storm and flood of 1928 had a particularly disrrupting effect on the work of the Experiment Station at that time.

### RATE OF TREATMENT

Although we now know that organic soils and the organic components of mineral soils have a very great absorptive power for such metallic elements as copper, the upper and lower limits of treatment with such materials was deemed worthy of investigation in the early days of these responses. Thus by graded applications in box plots of about 1 2000 acre in size it was found that bean plants would tolerate quite well applications of copper sulfate or manganese sulfate up to 10,000 pounds per acre as well as zinc sulfate in similarly high amounts if well mixed with the topsoil and allowed to stand a few days before planting. In addition to the "buffering" effect of the organic matter in the soil it must be remembered that our typical Everglades peat is directly underlain with lime rock and the soil has a high calcium content in consequence thereof. This, of course, adds very substantially to the absorbing or retaining power of this soil for elements such as copper, manganese, zinc, and boron which are found to leach only very slightly from it—even less, apparently, than phosphorus and potassium. Their actual availability for the use of plants under such conditions, is, of course, another question that depends very much on the reaction (pH) of the immediate soil environment as well as the ability of the individual plants (their "Feeding Power" as Dr. Truog has so well called it) to absorb their requirements from the form in which such elements are to be found in the soil.

### SOIL TESTING

In view of the mounting cost of fertilizer materials and the maintenance of a normal fertility level in the soil, the need for as much help as possible from soil and tissue testing in determining optimum applications becomes even greater with the advent of a whole series of trace elements into our soil fertility picture since, almost without exception, they are much more expensive than the so-called major elements.

Companion information in this same field of which we also have so little and need so much, is the composition of the plant material itself not alone in terms of what it takes to make a maximum growth or weight yield but also in terms of what composition individual plant materials should have in terms of these several elements to be of maximum value as a feed for animals and as food for man. This should well give a second basis for the future calibration of testing methods, both soil and tissue, if they are to be of maximum assistance.

Since we have come to recognize so fully the very great importance of many of the so-called trace elements to the health and growth, alike, of plants, animals and man during the past quarter of a century it would seem the service of future research in this field to the cause of plant, animal and human health would

be much greater if it were set up in such a way as not only to enlarge our understanding of the importance and function of each element but also arranged, and extended if need be, to include ways and means of routine soil and tissue testing to develop a system of protective information, of an Extension nature if you please, against the tragic losses that can follow the use of too much as well as too little of any or all of these secondary elements in a particular situation.



Figure 1.—The native sawgrass (Cladium sp.) from which the great mass of Everglades peat was largely formed. Jimmie Seal, Jr. in photo taken out in the Southeast Section of the Everglades Experiment Station on Feb. 12, 1928.



Figure 2.—Sugar Cane, U.S. 663 Left—Check (no treatment) Right—Copper sulfate 30 lbs. A.



Figure 3.—Left—Check (no treatment and no plants)
Right—Copper sulfate 30 lbs. A.
Rear—Crotalaria retusa
Middle—Crotalaria juncea
Front—Clitoria ternata



- Figure 4.—Red beets

  1. Copper sulfate
  2. Manganese sulfate
  3. Compost
  4. Check (no treatment and no plants)



- Figure 5.—Rape
  1. Copper sulfate
  2. Compost
  3. Manganese sulfate
  4. Check (no treatment)



Figure 6.—Another view of the remarkable response in sugar cane (Variety U.S.1639, left and U.S. 1637, right) to treatment of raw, Everglades peat with copper:

Below: general soil treatment with phosphate and potash but no copper, the plants on the copper-treated plots (closeup above) showing over the back-stop.

Above: same varieties of cane and same general soil treatment but with copper in addition. These two rows ran across five different soil treatments, including, of course, the check. These photographs taken about two and one half months before the great storm of September 16, 1928.



Figure 7—Response of sesbania, one of South Florida's most popular and useful leguminous cover crops, to treatment of freshly broken Everglades peat with 30 pounds of copper sulfate per acre in the row. Inset shows plants of the same age on check plot that had received no copper. Photo taken 80 days after planting.



Figure 8.—Pangola grass on raw sawgrass soil showing early stages of response. Plot in foreground received no copper and plants growing largely on the cuttings died out later. Plot immediately to rear received copper. Growth started strong and continued so.

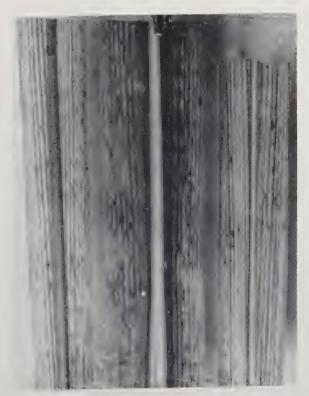


Figure 9.—The appearance of copper deficiency on the foliage of sugar cane variety Coimbatore (Co.) 281, having much similarily to a mosaic pattern.



Figure 10.—Sugar cane, variety Co. 281 on freshly broken sawgrass land, Check (untreated).



Figure 11.—Same as Figure 10 but the raw, peat soil given a light treatment with creosote and worked into the top six inches.

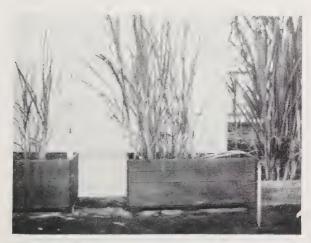


Figure 12.—The effect on growth of Co. 281 sugar cane in Everglades peat of continuous contact with a parent stool growing in soil fully treated with copper under greenhouse conditions:

Right—Parent stool
Center—Cane from stem "layered" in uncoppered soil
Left. Cut ease planted in uncoppered

Left—Cut cane planted in uncoppered soil



Figure 13.—Cane varieties from cut seed pieces in soil treated with Cu-P-K just prior to planting. Left-D-117 Center—Crystalina Right—Co.281



Figure 14.—Same general soil treatment as in Figure 9 but with Co. 281 stems layered into the soil from which very superior growth is developing.



Figure 15.—Duncan grapefruit on sour orange stock at about one year of age (Everglades Peat):

Left—Check (no treatment)

Right—Copper sulfate



Figure 16.—Villa Franca lemon on sour orange stock at about 17 months of age (Everglades Peat):

Left—Check (no treatment)

Right—Copper sulfate.

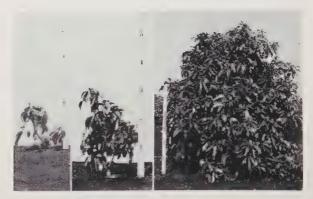


Figure 17.—Collinson avocado (Everglades Peat):
Left—Check—at about 1 yr. of age.
Middle—Copper sulfate at 1 yr.
Right—Copper sulfate at 28 mo.
Note: Check plants all dead at time of this later photo.

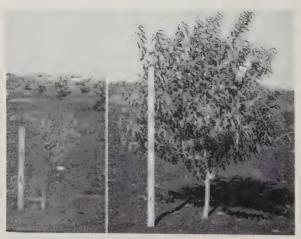


Figure 18.—Jewel Peach at about 16 months:

Left—Check (no treatment)

Right—Copper sulfate

(Everglades Peat)

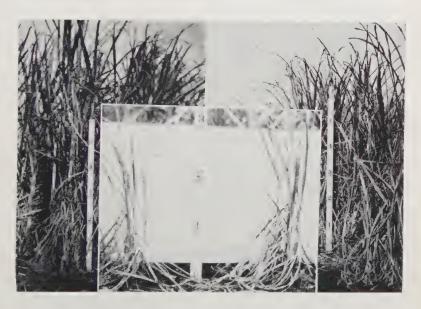


Figure 19.—Response of sugar cane, Variety Co. 281, to treatment of badly burned Everglades peat with sulfuric acid or with acid-producing sulfur to release manganese to the plant. Parker area near Moore Haven.

Left: Sulfur Center: Check Right Sulfuric Acid

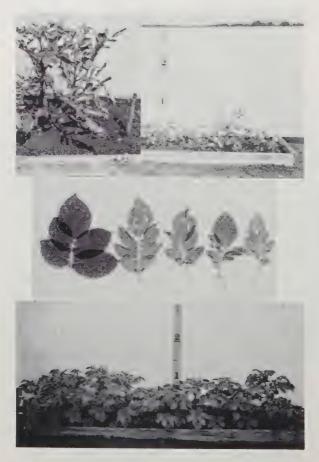


Figure 20.—Response of the Irish potato to treatment of badly burned peat soil. Top: Check plot and closeup of single plant. Center: Injured foliage series from left—normal, to right—colorless and nearly dead. Bottom: Normal growth of potatoes where fertilizer treatment included a generous quantity of manganese.

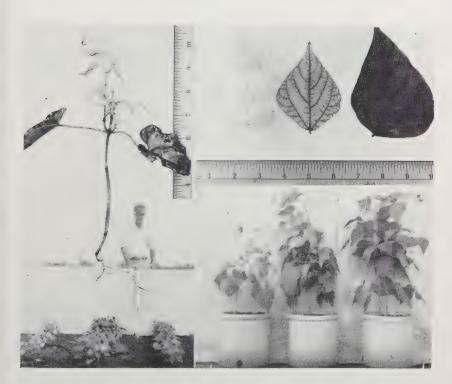


Figure 21.—Upper left: A typically chloratic bean plant due to manganese deficiency. Upper right: Bean foliage series showing range of manganese deficiency effect. Right—normal, Center—badly affected, Left—extremely chloratic and dying. Lower left: Response of beans to treatment of soil with high pH. (Maloy area, Dr. J. L. Seal in photo) Left—check untreated, Center—Copper, sulfur P<sub>2</sub>O<sub>5</sub> and K2O, Right—sulfur only. Lower right: Beans on "beansick" Pahokee soil. Left—check, untreated, Center—Superphosphate, Right—Manganese and superphosphate.

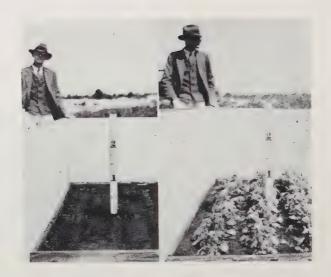


Figure 22.—Response of radishes to treatment of burned soil. Left: Check, no treatment, no plants. Right: Treatment with manganese and sulfuric acid. H. H. Wedgworth, Plant Pathologist at Everglades Experiment Station at that time, in photo (Feb. 26, 1931).

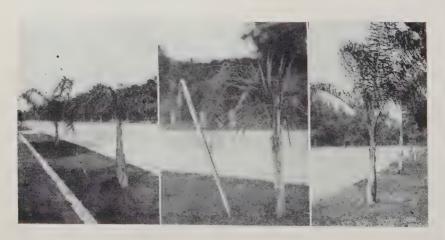


Figure 23.—Cocos plumosus palms in high lime soil along S. Third Street in Palm Beach failing because of the unavailability of manganese under such conditions of high pH. Center is a closeup of a palm typical of those found on either side of the street, left and right.



Figure 24.—Closeup of Cocos plumosus palms on one of the large estate plantings in Palm Beach where failure is also due to the high lime content in the soil.



Figure 25.—Royal palm failing badly, left, in the municipal area of Palm Beach where it had been planted in a soil containing too much free lime; also, right, on one of the larger estates where one of the "key figures" in its landscape architecture was dying for want of manganese at the time of the photo.



Figure 26.—"Fishtail" palm, growing quite close to the Cocos plumosus of Figure 24 and under essentially the same soil condition, is failing for the same reasons—unavailability of manganese under such high lime conditions in the soil.

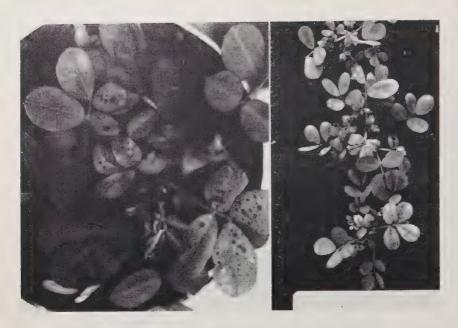


Figure 27.—Little Spanish peanuts growing on untreated Everglades peat showing extreme rosetting in all plants with foliage off color, leaves badly spotted and central growth in most of them nearly dead.



Figure 28.—Response of Little Spanish peanut plants to soil treatment with copper and with a combination of zinc and copper (sulfates). Left: check, no treatment; Center: Cu-Zn combination, the defoliation being due to normal ("early") maturity; Right: copper only, heavy with foliage due to late start and late maturity.



Figure 29.—Closeup view of the peanut plots involved in the copper-zinc response: Foreground, left—copper, zinc, caustic lime and manure. Center—manganese, zinc, caustic lime and manure. Right—copper, manganese, zinc, caustic lime and manure. Background, center—check, no treatment. Note: the mulch covering (sawgrass straw) on half of each plot represents another phase of the study—an effort at lowering the soil temperature at the surface.

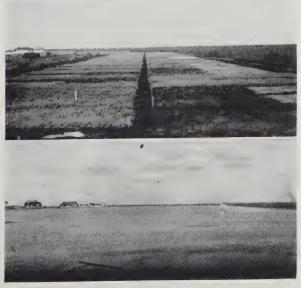


Figure 30.—General view, before (above) and after (below) the storm of 1928, of the series of peanut plots receiving single and all possible combinations of five different materials—copper, manganese, zinc (all as sulfates), caustic lime and manure. Photo taken from essentially the same position in both instances, i.e. on what was then the South Dike of the Experiment Station. Note that in the latter photo only the tops of the stakes along the central alley are showing though photo was not taken until about two weeks after the storm.



Kight center, copper sulfate. Left center, copper and potash. Left, copper, potash and superphosphate. copper, potash and superphosphate. Right center, copper and potash Right, copper, potash and super Left, check, no treatment. Left center, copper sulfate. Right, copper, potash and superphosphate. Leit, copper suitate and superphosphate.

Senter, copper and potash



Figure 32.—Beggar weed plants the check plot of the trace element series where three of the original planting rows were replanted and a row seeded in each of the middles to conform with the planting on the plot that received the earlier copper treatment, Figure 33, below.



33.—Beggarweed Figure in second planting on copper treated plot to show residual values. Three rows with good growth are in the original lines of treatment with copper sulfate while the two rows that are failing completely have been planted entirely out of contact with this copper. These little plants are dying for lack of copper though the soil in which they are trying to grow is completely filled with strong healthy roots (see rape roots of Figure 34) from the plants adjacent which have access to the copper that is residual from the earlier treatment.



Figure 34.—Block of soil containing rape roots as excavated from one of the copper treated plots from the row (looking down into plant stubble) to somewhat more than half way across the middle to the row adjacent. This is to show the complete manner in which the roots of healthy, copper-treated plants completely permeate the soil when growing as normally as the beggar weed plants of Figure 33.

# RESPONSES OF PASTURE AND FIELD CROPS TO TRACE ELEMENTS ON MINERAL SOILS IN FLORIDA

# ROGER W. BLEDSOE\*

Visual deficiency symptoms have been used primarily as a guide to the adequacy of trace elements in the nutrition of pasture and field crops grown on the mineral soils of Florida. Such symptoms may develop only when the deficiency is severe. Chemical analysis of soil and plant may be of value in determining the cause when plants show deficiency symptoms. However, if the plant shows no deficiency symptoms such analysis may be of questionable practical value in determining whether an element is limiting in the nutrition of the plant. Soil analyses do not show the availability of the trace elements. The concentration of an element within the plant may not serve as an index of deficiency because deviation from the normal might occur only when the deficiency is extreme. Furthermore, with most pasture and feed crops the concentrations of trace elements required within the plants have not been established.

# PASTURE PLANTS

Results by Killinger, et al., (11), indicated trace elements to be beneficial in the establishment of Dallis, carpet, Bermuda, and Bahia grasses on certain virgin flatwoods soils only when used with lime and a complete mineral fertilizer. Copper appeared to give the greatest growth response followed by manganese, zinc, and boron in decreasing order. The trace elements did not have any significant influence on yields after the grasses were established.

Hodges, et al., (8-9), reported similar results with grasses. A combination of three elements, copper, manganese and zinc, gave yields superior to those where only one element was applied. Common Bermuda did not respond to applications of trace elements while the response by common Bahia was less than that of carpet and Pangola grasses. The growth and survival of Pangola grass was distinctly improved when only copper was applied. A rate of 5 pounds per acre of copper sulphate was as beneficial, in some cases, as higher rates.

Boron has been shown frequently to improve seed setting of clovers when grown on the mineral soils. Killinger, et. al., (11), observed boron deficiency symptoms of California burclover when grown in the absence of boron fertilization. Seed setting of Black medic and Annual sweet clover was greatly improved when boron was applied (14). Clovers have not re-

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sponded appreciably to applications of other trace elements with the possible exception of zinc (3).

Hodges, et al., (10), reported the growth of common and Kobe lespedezas was considerably improved when fertilized with copper, zinc, manganese, and borax as compared to the notrace element treatments. However, trials with other legumes showed no response to trace elements.

The importance of trace elements can not be minimized where needed for the growth of pasture plants on mineral soils. Crop failure may result on those soils naturally deficient in one or more of the trace elements as well as on alkaline or overlimed soils, unless the needed elements are added regardless of the quantities of nitrogen, phosphorus, and potassium applied. Where needed for pasture plants the following rates per acre are generally recommended: 15 pounds each of copper and manganese sulfates, 15 pounds of zinc sulfate, and 10 pounds of borax.

#### FIELD CROPS

In 1935 Barnette and Warner (2) described the visual symptoms of white bud of corn and demonstrated it was due to a deficiency of available zinc in the soil. In 1936 Barnette, et al., (1) described zinc deficiency symptoms of velvet beans, cowpeas, and millet. Oats grown on land which had produced white bud of corn responded favorably to the application of zinc sulphate with increased yields, while peanut yields in some cases were increased but symptoms of malnutrition were not observed with either crop. Yields of sugar cane, Napier grass and crotolaria were likewise increased by the application of zinc sulphate but deficiency symptoms were not observed. Thus, the value of zinc for preventing the development of plant disorders and for increasing plant growth was established.

Results by Barnette et al., (1) showed that "resting the land" or permitting it to lie fallow to volunteer weeds and grasses had reduced materially the percentage of white bud corn plants of experimental plots. The incorporation of a relatively heavy planted crop of crotolaria had not been as effective as that of native cover crops in reducing white bud of corn. On plots planted to corn and peanuts annually the corn showed by far

the largest percentage of white bud.

Results by Rogers, Gall and Barnette (13) show that the dry matter of weeds collected from plots "rested" for 2 years averaged 140 p.p.m. of zinc; that of *Crotolaria spectabilis* Roth. planted annually 8 p.p.m. The dry matter of weeds and grasses collected from plots "rested" for 1 year averaged 70 p.p.m. of zinc, that of 3 species of crotolaria planted in plots in a 2-year rotation with corn and peanuts 21 p.p.m. The authors state that the data indicate weeds and volunteer grasses are able to absorb much larger proportions of zinc than are planted land covers

and apparently make available sufficient zinc to prevent the de-

velopment of white bud of corn.

The author has observed white bud of corn grown on mineral soils in various areas of the state. Some varieties of corn, for example, Dixie 18, appear to be more sensitive to available zinc supply than other varieties. The occurrence of white bud appears also to be closely associated with climatic conditions. Some seasons the disturbance is far more prevalent than that of other years in the same region. However, in many instances the young plants seem to recover rather rapidly, even without the addition of zinc, and the yield of corn is thought to be little affected.

Nutritional disturbances attributable to zinc deficiency, other than that of corn, are rarely noted in field crops grown on mineral soils. However, specific deficiency symptoms of value for diagnostic purposes have not been established for many of the field crops. When plants are grown under field conditions the symptoms may be difficult to recognize, not visible, or masked by other plant ailments. Zinc deficiency symptoms of peanut have not been observed on field grown plants, while symptoms are very distinct when plants are grown under controlled conditions.

The author demonstrated zinc deficiency of peanut when plants were grown under controlled conditions and supplied repurified chemicals and redistilled water. Symptoms of zinc deficiency were evident within 14 days on the Holland Station Runner Jumbo variety and 21 days with Dixie Runner variety after zinc was withheld from roots of plants. The first evidence of a disturbance was retarded growth and reddish coloration of stems and petioles. The leaf pattern might be described briefly as "little leaf" which is especially evident in the terminal growth where it appears first. The foliage is small, narrow, crinkled, and chlorotic at tips. Midrib and major veins of older leaves have a prominent light color. The blades are thick and leathery and wrinkled along the midrib. In advanced stages the midrib breaks down and necrotic areas appear irregularly over the leaflet's surface. The pattern progresses from terminal to basal portion of plants with age.

Distinctive symptoms of copper deficiency in field grown plants on mineral soils have been reported in only a few cases. However, because of the low content in soils of some areas copper is often suspected of being the trace element most likely

to be a limiting factor in plant growth.

Hodges et al., (10) reported that oats grown on Portsmouth fine sand, mucky phase, developed mineral deficiency symptoms which were completely remedied by the application of 15 pounds of copper sulfate per acre. There was no evidence of copper deficiency in oat plants grown on the adjoining prairie phase of Portsmouth fine sand.

Harris (4) described a nutritional disturbance in oats grown on Arredonda loamy fine sand at Gainesville which could be cured only by additions of copper salts. A very small amount of copper chloride (2 pounds per acre) was beneficial and had considerable residual effect (5). High applications of nitrogen accentuated the abnormality and caused a decrease in grain yields. The yield of shelled corn was increased 20-23 per cent in consecutive years when copper chloride was applied at 10 pounds per acre even though symptoms of a deficiency were not evident. Yields of barley, wheat, and cowpeas were increased also by applications of copper while the yield of rye was not affected. (6)

Harris (7) describes a nutritional disorder of peanuts, when grown on the same location as that of crops mentioned above, and demonstrated its control by the use of copper salts. Exceptionally small amounts of copper chloride applied as a spray had a pronounced influence on yields. Affected plants had small, irregular terminal leaflets with small yellowish-white spots, marginal necrosis and some interveinal chlorosis.

Copper deficiency symptoms of peanuts grown in nutrient solutions in the greenhouse, as demonstrated by the author, were somewhat different from those described in field grown plants. Thirty days after copper was withheld from the roots the young leaves of some plants withered suddenly without any other symptoms. Terminal leaves were small and interveinal chlorosis occurred on the leaflets of the second or third leaf below the growing tip of some plants. Stem tips ceased to grow but stems were not discolored. In the more advanced stages the young growth withered and died on all plants.

In a field test the author observed a nutritional disturbance, similar to that reported by Harris (4), in young peanut plants of three of six replicated plots. Copper-sulfur dust was applied to all plots. The disorder was corrected and there was no sigficant difference in yields. Yields of peanuts grown near Live Oak were increased by approximately 30 per cent by applications of copper-sulfur dust. Treatment of other trace and major elements had little influence on yields (unpublished data by the author and Mr. Fred Clark). Results by Killinger, et al., (12) and unpublished data accumulated by Station workers during the past several years show that yields of peanuts dusted with copper-sulfur are usually superior to those dusted with sulfur. It is suspected that the added response to copper-sulfur dust is in part nutritional.

Severe symptoms of manganese deficiency are rarely observed in farm crops grown on the mineral soils. Perhaps that is because a majority of the soils used in the production of farm crops are acid in reaction while manganese deficiency is usually associated with soils of a neutral or alkaline reaction. Under some circumstances, slight deficiency symptoms may appear, especially during prolonged periods of dry weather and then disappear after heavy rains. However, it is frequently difficult to distinguish between manganese and iron deficiencies, since

in both cases the veins are green. Manganese deficiency symptoms are sometimes observed in over-limed areas.

The author demonstrated manganese deficiency symptoms of the peanut when plants were grown in nutrient solutions. The deficiency appears first as interveinal chlorosis in tip leaves and then moves progressively toward leaves at base of plant. Chlorosis starts frequently at the base of a blade and progresses toward leaflet tip. The green color of veins is not prominent. Later the entire leaflet turns yellow and necrotic spots appear irregularly over the surface but rarely at leaflet margins until late stages. Large areas of leaflets then turn brown and leaves drop prematurely.

Chlorosis due to iron deficiency is frequently observed in lawn grasses, especially in centipede and St. Augustine. It is rarely observed in other crops grown under field conditions.

Responses to application of molybdenum to field crops grown on mineral soils have not been reported. The author observed evidences of molybdenum deficiency of peanuts during two consecutive years when plants were grown on plots at Marianna to which no molybdenum had been applied. The leaves of untreated plants were yellowish to pale green as compared to the dark green leaves of treated plants. The symptoms occurred during the early growth stages and later disappeared. Yields of those plots were not significantly lower than those of plots to which molybdenum had been applied. Florida Station workers have observed similar symptoms in peanuts, cowpeas, and crimson clover during early growth stages which later disappeared. Yield responses were not obtained where molybdenum had been applied.

Symptoms attributed to boron deficiencies of crops grown under field conditions have not been reported. However, flue-cured tobacco fertilizers usually contain approximately 2.5

pounds of borax per ton of fertilizer.

In general the mineral soils used in the production of pastures and field crops are very sandy, very low in organic matter, and have a low level of fertility. Mineral fertilizers, where used, are applied at low rates. Sprays and dusts which might contain some trace element are rarely applied to pastures and field crops. The practice of allowing land to lie fallow to volunteer natural cover crops is decreasing rapidly. Planted cover crops are being used more extensively. It would appear that on such areas any intensive farming practices which would be a soil depleting program could soon lead to difficulties. If climatic factors, soil moisture, and major elements supply, which are frequently the limiting factors in field crop production, are particularly favorable for plant growth it is quite possible that many of the otherwise adequate soils could become deficient as a source of trace elements necessary for maximum yield production.

During some seasons deficiency symptoms of trace elements

are more prevalent than those of other years. Deficiencies are often manifested at early stages of plant growth, or during periods of dry weather, and then later disappear. Stunted growth attributed to other plant ailments is often thought to be associated with trace element deficiencies. Results of studies to date indicate that with the exception of a few areas there is no critical shortage of trace elements in the mineral soils of the state. However, they also indicate that at times the availability of trace elements may be below the optimum physiological requirement necessary for maximum growth and yield of plants. In such areas the producer of crops and livestock must be aware of the importance of the trace elements, for to him, it could mean the difference between success and failure.

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# TRACE ELEMENT RELATIONSHIPS IN FLORIDA VEGETABLE CROPS ON MINERAL SOILS

# J. R. BECKENBACH\*

#### INTRODUCTION

Much of Florida's vegetable crop production—especially the fruit crops such as tomatoes, peppers, eggplant, squash, etc.—is located on relatively flat sandy soils of the poorly drained sands. Water control, both drainage and irrigation, are essential to production on such soils. Vast areas of mineral soils are under such control in the important areas of the state.

Some of these areas are natively good to high in soil reaction; the marl soils of the Homestead area having a pH in the range of 8.0 and a bit higher, and Parkwood and related soils ranging from pH 5.5 on up to slightly above 7.0. Other soils utilized extensively are natively very acid, however, Leon sands, for ex-

ample, natively range from pH 3.9 to 4.4.

All have been heavily leached over the centuries, and those of low pH are very low in soluble salts, including both major and trace element bases. When these are limed and fertilized for vegetable crop production, this lack of trace element bases becomes apparent. For this reason, the magnesium carrying dolomitic limestone has proven better than high calcic lime, and basic slag has usually proven superior to both. The manganese content of the slag is of unquestioned importance in making these comparisons.

Magnesium, manganese, iron, zinc, copper and boron have all been found to be deficient in certain of these limed soils. On an emergency basis, deficiencies of all may be at least partially corrected by their addition to sprays, so that we know that leaves can absorb them. Incidentally, Florida has pioneered in this

line of research endeavor.

Iron and boron are rather dangerous when applied as sprays with some crops because of relatively low requirements and because tolerance limits are narrow. There is evidence that mixtures of trace elements are somewhat safer than single element sprays in some cases.

# PRESENT STATUS

Generally speaking the present status of the problem of trace elements on vegetables in Florida is something like this:

Magnesium. On soils needing lime, the use of dolomitic limestone takes care of the situation. On soils deficient in mag-

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nesium but with adequate calcium and of desirable pH range, Magnesium sulfate is used in the fertilizer, supplied in definite ratio as magnesium oxide.

Manganese. This element, as the sulfate, is used directly on the marl soils of the Homestead area, in annual quantities up to 100 lbs. per acre. It may also be used in the fertilizers on sandy soils of naturally high pH or that have been recently limed. In addition, it may be safely included in a spray application in quantities up to 4 lbs. per 100 gallons of spray.

Zinc. This element, again the sulfate, is often added to the spray, at 2 lbs. per 100 gallons. Response to zinc has been very definite on some vegetable crops. Toxicity symptoms appear quite readily if too much is used. Actually, no additional zinc sprays are required on crops which are sprayed with the new zinc fungicides—in fact, zinc toxicity has been known to develop on tomatoes and other crops when such fungicides are used exclusively.

Copper. Prior to the introduction of the zinc fungicides, none of the vegetable crops on mineral soils developed copper deficiency symptoms, or at least copper deficiency was never a major problem on such soils. Crops such as tomatoes, peppers, potatoes, etc. regularly received copper fungicidal sprays. Apparently the older agricultural soils had adequate copper residues to carry crops through the first several years of zinc fungicides, but copper deficiencies appeared rapidly on virgin soils brought into production and sprayed only with zinc fungicides. Whether zinc additions actually intensify copper deficiencies, or whether the copper need is relatively high in its own right has not been determined. In any event, copper nutritional or fungicidal sprays are required on most vegetable land newly brought into production. To some extent, definite ratios of copper in the fertilizer are used.

Iron. This metal, as the ferrous sulfate in spray applications, will quickly correct the deficiencies sometimes encountered on limed soils. It has not been possible to establish an absolutely safe spray strength, however. One lb. to 100 gallons will usually relieve the deficiency, but sometimes marks tomato or other fruits to an economically damaging extent. There seems to be less tendency for such damage to appear when other trace elements are included in the spray mix. Apparently the iron carbamate fungicides are safe on these crops, but they do not have much effectiveness against most major vegetable diseases in Florida. Where they are used, a definite nutritional response is sometimes evident.

Boron. Borax is the common source of boron used, and may be included in the fertilizer for crops with a high boron requirement, such as broccoli, cauliflower, lettuce and cabbage. An an emergency basis, borax is sometimes applied as a spray or drench. The upper safe limits have not been entirely established, but up to 2 lbs. per 100 gallons have been applied in this manner without damage.

# FUTURE RESEARCH NEEDS

The research approach of the past—that of testing out trace element additions by spray or in fertilizer to cope with emergency problems—is not comprehensive enough to satisfy actual commercial needs in Florida. Several trace element deficiency problems which caused tremendous economic losses have been solved in this manner. Among these are "cracked stem" of celery which is corrected by additions of borax, copper deficiency on the organic soils of the Everglades, and zinc and manganese deficiencies on a variety of vegetable crops grown on a wide range of soil types, to mention a few. Iron and magnesium deficiencies have also been recognized and corrected, but these conditions have been of less economic consequence in the vegetable producing areas.

There are still physiological disorders of vegetable crops of major economic importance which must be solved. The efficient utilization of certain nitrogen source materials is a practical, major problem here in Florida. The adjustment of pH, the method of water control (which is basically an aeration problem) and the balance of trace and major elements available are felt to be related to this nitrogen problem. Blossom-end rot of tomatoes and peppers and black-heart of celery are partially solved problems which need investigation as to trace element effects in relation to pH control and irrigation methods.

There is a fundamental background of research in plant nutrition to which we must tie our program. Physiologists have demonstrated that aeration of the soil solution influences manganese requirement; that the manganese—iron balance is of nutritional importance; that nitrogen source affects the need for trace elements and the balance required among trace elements. Length of day and intensity of sunlight enter the picture—in fact, trace elements are essential to all basic plant processes and need investigation from that point of view.

It is my feeling that we in Florida, of all states, need to make provision for fundamental research involving trace elements in plant nutrition. Our methods of irrigation, the length of day during the growing period and the soil types which we farm all influence the balance of trace and major elements required. To some extent at least, these problems are peculiar to Florida, and it is our urgent problem to solve them.

The vegetable producers of the state are being forced to move on to the less desirable soil types. Soil areas most suitable for vegetable production are now in general use; future expansion must be on the acid, poorly drained sands. Vegetable crops cannot be grown on such soils in anything like our economical manner until they are drained and limed so that the first requirement is to alter the soil to a condition more nearly comparable to that of the more suitable soils. Drainage and liming do this to some extent; certain physical characteristics cannot be so altered in any practical way, and we must learn to adapt to them. It is in this adaptation that we need to investigate the complex, controllable problems involving trace elements, irrigation methods, nitrogen source materials and other factors.

It would seem desirable and necessary that we here in Florida do some fundamental work on the nutritional relationships involving trace elements. The recognition of trace element deficiency symptoms, and the development of means for correcting these, has been a great step forward. It has resulted in important commercial advances in vegetable production in Florida. The reported literature on these phases is vast, and research on a field scale is quite general.

Only a few restricted laboratories are busy investigating fundamental nutritional relationships among trace elements and between trace elements and other factors that influence their need in plant nutrition. I believe that the growers of Florida would benefit very greatly if we could establish a program here to pursue such lines of investigation. I have reason to believe that many of our problems involving the quality of our vegetable crops could be solved—or at least understood—by investigating them in this manner. Trace elements, like other plant nutrients, have certain specific functions in plant nutrition. There are great gaps in our knowledge of these functions. In addition to these direct influences on plant growth, the physico-chemical properties of ions in complex water solutions are such that it is impossible to approach some of these problems by varying the concentration of only one salt in plant nutritional studies. We have great need to study some of these things, since daylength, irrigation methods, drainage, temperature and other variable factors are of practical importance here. This approach to the problems in the field of future research on trace elements could be expected to result in important commercial gains by our vegetable growers.

# THE PROMINENT ROLE OF THE SO-CALLED TRACE ELEMENTS IN THE RECENT REHABILITATION OF FLORIDA'S CITRUS INDUSTRY

# A. F. CAMP\*

Inasmuch as Dr. Camp's discussion of the comparatively recent rejuvenation of Florida's Citrus Industry very largely through the judicious use of certain of the trace elements was almost entirely on the basis of a large series of excellent slides and no manuscript for the record was provided, this important subject can be reported only very briefly at this time.

Emphasis was given, of course, to the observations that had been made for many years of the quite appreciable benefits that always seemed to follow the liberal application of such natural organics as dried blood or tankage, the extent of certain physiological responses appearing to depend largely on the amount of the application even to a point where too much nitrogen obviously was suplied.

General decline continued in a large percentage of the groves of the State, however, until the first trials with zinc in Gainesville, as reported in 1933, proved so extremely beneficial in curing, and of course preventing, the so-called frenching of citrus as well as the rosetting of pecan and the bronzing of tung trees. The results of zinc treatments were so dramatic that almost within the same season it became a general field practice.

Studies of the use of copper for the control of "dieback" or "ammoniation" in citrus revealed its complete effectiveness only a year or two later and both elements were promptly recognized as essential, each supplementing and neither replacing the other where both situations were involved in the grove. The general use of manganese rather quickly developed as did also the appreciation for the need for boron in restricted areas. Throughout all these studies iron deficiencies were recognized, as in the citrus groves of the East Coast Area, but its effective application has been found very difficult.

Continuing studies, therefore, are concerned largely with finding more effective, as well as more economical forms of these elements and methods of application as well gaining a better insight not only into their effect on gross yields but the composition of the fruit as well, especially from the standpoint of their use as human food. Ed.

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# TRACE ELEMENT CONTENT OF LEAVES FROM TUNG ORCHARDS

### MATTHEW DROSDOFF<sup>1</sup>

Inasmuch as no manuscript was submitted by the author it can be reported on only briefly at this time. However, it was published in Soil Science Vol. 70, No. 2, pp. 91-98, 1950.

It was noted that trace element deficiencies in relation to the growing of tung trees in the United States are particularly conspicuous in the lighter textured soils of Northwest Florida where the major acreage of this crop is grown.

Methods of foliage sampling, sample preparation and of analysis for five of the more important trace elements were described in brief detail and results reported on the basis of parts per million of the various elements in terms of dry matter involved.

The brief summary of this paper as published in the above referred to volume of Soil Science follows: "The zinc, copper, manganese, boron, and iron contents of representative tung-leaf samples are discussed in relation to the kind of soil on which the trees are growing and the kind and amount of fertilizer applied. Under all conditions observed, the range in zinc content of tung leaves was found to be 10 to 229 ppm., copper 2.5 to 12.4, manganese 25 to 2,884, boron 38 to 226, and iron 35 to 92."

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# MINOR ELEMENT DEFICIENCIES OF DECIDUOUS FRUITS AND NUTS

# G. H. BLACKMON\*

There are certain minor elements which must be provided for the best growth and production of deciduous tree fruits and nuts grown on most soils in Florida. The crops which will be discussed are the pecan, peach, pear and cultivated persimmon. Of these the pecan is the most important commercial crop in Florida, fol-

lowed in order by peaches, pears and persimmons.

The need for zinc in the growth and production to correct rosette of pecans in the South was first shown about 1932 by J. R. Cole, Pathologist, U. S. Pecan Field Station at Albany, Georgia, but at that time he was stationed at the U.S. Pecan Field Station, Shreveport, Louisiana. This was the year that Harold Mowry, Horticulturist, later Director, of the Florida Agricultural Experiment Station, showed that zinc was necessary to correct bronzing of tung trees.

Soon after these findings, work was started in Florida by the author, who investigated the zinc requirements of pecans in various parts of the state. It was shown that nursery as well as orchard trees must have zinc applied for growth to be free of rosette if there is not already sufficient zinc available to the

plants.

In these investigations it was found that pecan trees would respond to zinc applied to the soil in which they were growing, if needed, in all instances where such soils were otherwise adapted to pecan growth. Rates of zinc applied as zinc sulfate were worked out for several varieties of pecans in different parts of northern and western Florida. It was soon determined that, in cases of severe rosette, about five pounds of zinc sulfate applied to the soil in the spring would usually correct the disorder and, in the second year following application, the trees would begin to make normal growth. After this, about two pounds zinc sulfate annually per tree would generally provide sufficient zinc for normal growth in bearing trees. However, where bearing trees showed slight to moderate amounts of rosette, the two pound annual application was generally all that would be necessary for maintenance of normal growth and production.

During these experiments zinc oxide applied to the soil as the source of zinc was tested. It was found that zinc oxide proved satisfactory in causing trees to resume normal growth but required one or two years longer for the same degree of re-

covery than did zinc sulfate.

Zinc sprayed onto the foliage of pecans was developed as a satisfactory method of correcting rosette, by Cole and others.

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This proved effective also when tested in Florida. This is a very efficient way of applying zinc, since zinc sulfate can be added to the regular pecan sprays used for the control of insects and diseases, or it can be applied alone. Generally, four or five pounds of zinc sulfate to each 100 gallons of Bordeaux or other spray mixtures will correct rosette when sprayed onto the leaves in June. If zinc sulfate is used alone, the same amounts would be mixed with 100 gallons of water to which would be added about three pounds of hydrated lime.

Rosette is not a problem now in well-managed pecan orchards. Zinc is applied in some manner whenever needed. Many growers make a practice of applying zinc sulfate annually in the fertilizer as a maintenance program.

In sand and water cultures it was shown that boron was necessary for normal growth of pecan seedlings. The seedlings grow normally with 0.5 ppm of boron added with the nutrient solutions. Toxicity developed in the leaves of the plants with greater amounts of boron applied. It was found that there was a greater utilization of nitrogen also when the boron was added to the nutrients.

Following this work, borax was applied to 17 year old, lowyielding Stuart trees on the Experiment Station Farm in 0, ½, 1, 2, 4, 8, and 16 pounds per tree. The amount of boron present in the soil before the borax applications, was determined by H. W. Winsor of the Soils Dept., Florida Agricultural Experiment Station. The soil contained relatively low amounts of native boron, ranging from 0.09 to 0.18 ppm. The boron applied was readily taken up by the trees as shown by leaf analysis, but no benefits were obtained with any of the amounts of borax applied. However, toxicity showed up in the foliage of those that received four pounds and more of borax. The experiment was replicated four times and on two of the replicates the applications were repeated the second year with similar results. The tests were made in 1945 and 1946, and in the first year following that of each treatment only those trees which received the 8 to 16 pounds of borax showed toxicity in the leaves. By the second year the leaves on these trees cleared up and have since remained in good growth.

Large-scale experiments were initiated in commercial orchards in 1948 following preliminary tests in 1947. In these the applications ranged up to four pounds of borax per tree. No toxicity developed in the foliage, but no beneficial effects on growth

and yields were obtained.

Magnesium, while not generally considered as a minor element, is included because there have been a few instances where it has been observed as lacking in pecan foliage. Tests have shown that trees will take up applied magnesium as revealed in leaf analysis but increased nut yields have not been obtained with its application.

Florida is not a large commercial peach producing state, but there are a few orchards of early maturing varieties and small home plantings in many parts of the state. A condition known as little-leaf was noted quite universally in various young orchards and yard trees in 1938. R. D. Dickey, Asst. Horticulturist, Florida Agricultural Experiment Station, and the writer set up experiments in 1939 to determine the cause of this disorder. Zinc, manganese and magnesium were applied to the soil singly and in combination in the tests. Zinc and manganese were also tested in foliage sprays. It was shown that little-leaf of peach in Florida was caused by insufficient zinc available to the trees. In these experiments the condition was corrected with zinc applied either to the soil or as a spray to the leaves.

R. D. Dickey, in experiments with Pineapple pears, showed that zinc will correct a certain physiological condition which appears in the leaves of the trees. Trees tested responded to zinc sulfate applied either to the soil or to the leaves in a foliage spray.

Mr. Dickey has also reported on a chlorosis in the cultivated persimmon (commonly known as the Japanese persimmon), which apparently is caused by a zinc deficiency. With properly timed applications, the disorder responded to zinc made available to the trees.

As an over-all picture, satisfactory growth and production of deciduous tree fruits and nuts in Florida will often require applications of one or more minor elements. Growers who are alert watch for symptoms of deficiencies and apply the elements when and where they are needed. This, together with a general maintenance program which includes the growing of adapted covercrops of legumes, and with additional adequate plant foods applied, have contributed to the production of these crops in Florida.

In presenting the paper, the different deficiencies were il-

lustrated with colored slides

# MICRONUTRIENTS IN SUBTROPICAL FRUITS

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The success or failure of subtropical fruits in Florida is determined to a large extent by the presence or absence of an adequate supply of the micronutrients. In spite of the extreme importance of these elements, there is very little known about the amounts of each of them necessary for the growth of these plants. A few of the more important plant species have already been subjected to investigation with regard to micronutrients. For many others, a cure-all spray has been developed which makes their growth possible. The soil in a large portion of the area suited by climate and elevation to the growth of subtropical fruits is highly alkaline and deficient in nearly all the elements except calcium. The soils of the remaining portion are sands

which are deficient in even this element.

The alkaline soils are located south of Miami. They are derived from an oolitic limestone which contains very few impurities. The mineral fraction of these soils is 90 or more percent calcium carbonate with the balance made up of silica and iron oxide. It is the organic fraction which makes it possible for these soils to be used for agricultural purposes. The raw rockland, recently scarified, will have a pH of 8.2. Nevertheless with proper management good plant growth can be obtained. Once there is some shade, organic matter will accumulate on the surface. If this layer of organic matter is not mixed with the soil by cultivation, it will eventually become acid. Surface soil samples taken from groves in the Redlands had a pH of 7.0 to 7.5. An occasional sample was even more acid. Some hammock soils which were purely organic had pH values as low as 4.3 This acid condition has no permanence, however. Even old land with a thick layer of debris will lose its ameliorating blanket when exposed to direct sunlight.

In other sections of the State, suitable to the culture of subtropical fruits, acid sands predominate. These present an entirely different set of problems than the soils in the vicinity of the Sub-Tropical Experiment Station. As a result, the problems connected with subtropical fruits in these acid sands have been somewhat neglected. The practices recommended for citrus culture have usually proved adequate in these areas. The Plant Introduction Garden of the Bureau of Plant Industry and the experimental farm of the University of Miami are also in the al-

kaline soil area, which is unfortunate.

At present avocados and mangos are the most important subtropical fruits in Florida. The micronutrient requirements of these trees have been studied in some detail in the field and under controlled conditions. Although both of these fruits are important in other countries and have been subjected to study in those

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countries, most of the work on nutrition has been undertaken in Florida or California. Papayas, guavas, and some of the lesser fruits have been subjected to preliminary investigation and are grown successfully. The pineapple has been thoroughly studied in Hawaii and Puerto Rico, but very little of the information obtained under those conditions is applicable to its culture in Florida.

Successful grove culture without the use of micronutrient sprays has not been possible in the Homestead area, since the organic nitrogen fertilizers are no longer available or prohibitively expensive. Backyard trees and an occasional pothole planting will succeed without these sprays but no extensive planting is known where the trees are in the best condition without such sprays. Favorable response has been obtained to nearly all of the elements except iron. Zinc deficiency was the first nutritional disease of avocados to be described. The latest to be described in the Homestead area is the result of boron deficiency.

Little-leaf of avocado, the disease caused by severe zinc deficiency, was first described by Coit (1) in California. A complete description of this disease was given by Parker (4) in 1936. Ruehle (5) recognized this deficiency in Florida in 1938 and corrected the trouble with a foliage spray containing 10 pounds of zinc sulfate and 5 pounds of hydrated lime in 100 gallons of water. Sprays of manganese and iron salts on trees in the same grove did nothing to improve the condition of the trees. Ruehle (5) observed that zinc deficiency symptoms were much more severe in dry seasons and in groves where inorganic sources of nitrogen was used in the fertilizer program.

Copper deficiency in avocados was reported by Ruehle and Lynch (6). This occurred on newly-cleared, acid, sandy soils in Highlands County. The trees were young and in the early stages of the disease, appeared starved. The old leaves became dull and the veins prominent. In the next stage, the old leaves were shed and the branch tips died back. Multiple budding was a common symptom. An application of copper sulfate to the soil at the rate of two ounces per tree was sufficient to correct the condition. The use of manganese sulfate or mixed fertilizer without copper aggrevated the condition. Bordeaux or a neutral copper spray was suggested as a remedy for the deficiency but was not tested.

Two varieties of avocado were studied in sand culture by Furr, Reece, and Gardener (2). They described nitrogen, phosphorus, potassium and magnesium deficiencies, as well as the micronutrient deficiencies boron, copper, iron, manganese, and zinc. In the relatively short time their experiment was carried on, severe copper and zinc deficiency symptoms as reported by Ruehle (5) and Ruehle and Lynch (6) did not develop. Iron chlorosis was severe, with the young leaves almost free of chlorophyll. In the absence of manganese the older leaves commenced bleaching between the veins. This first appeared as separate

spots but gradually only the veins remained green. The leaves also became chlorotic when boron was withheld. The leaves fired at the margins and dropped prematurely. New shoots were short with small leaves. At the end of the two years of the test, dieback was already commencing. This has not been reported under grove conditions. Recently Dr. Roy W. Harkness of the Sub-Tropical Station has found that darkening of avocado seeds was related to low boron content of the leaves. This condition was not found where the trees received boron as a soil treatment. Most embryos in seed of untreated trees were dead or injured; from the treated trees only half the embryos appeared defective.

Zinc deficiency in the mango was observed by Lynch and Ruehle (3). The symptoms were similar to those in the avocado. They were most severe after prolonged dry weather on trees that had been liberally fertilized. The leaves were small and thickened. In some cases they formed rosettes. The condition was corrected by a foliage spray containing 5 pounds of zinc sulfate and 2.5 pounds of hydrated lime in 100 gallons of water. At the last meeting of the Mango Forum, Dr. T. R. Robinson reported that fruit cracking of mangos of the Sandersha type was prevented by the use of borax at the rate of two ounces per tree on the sandy soils of the West Coast of Florida.

For the rest of some 1400 odd species of plants now growing at the Sub-Tropical Experiment Station, we have no very definite information. It is the practice to spray these plants several times during the year with a nutritional spray containing copper, manganese, and zinc. A typical spray mixture is suggested in the recently revised avocado bulletin, "Avocado Production in Florida," by Wolfe, Toy and Stahl, revised by G. D. Ruehle (7). They recommend three pounds of copper sulfate or the equivalent in one of the neutral coppers, two pounds of zinc sulfate, two pounds of manganese sulfate, and sufficient hydrated lime for their neutralization, in 100 gallons of water. It may not be advisable to include the manganese in the spray more often than once a year.

This nutritional spray is recommended for use on plants in the Rockdale soils. Recently it was used in the greenhouse on Macadamia seedlings planted in regular potting soil. These seedlings developed a severe chlorosis almost at once. The chlorosis was corrected by spraying with a weak solution of ferrous sulfate but the plants were considerably set back before the nutritional balance was restored. On the acid soils throughout the rest of the State, soil treatments seem preferable to nutritional sprays. The elements applied in this way are available to the trees but do not have to be applied at such frequent intervals.

It is impossible to overestimate the importance of the micronutrients in the growth of subtropical fruits. Because of the inherent nature of the soils in the areas suitable for the growth of these plants in Florida, most of the elements must be supplied by the fertilizer or nutritional sprays. On the alkaline soils, sprays have proved to be the only satisfactory method of application. On the acid sands, the required elements may be included in the fertilizer. The study of the problem of micronutrients in subtropical fruits has just begun, but it is a good beginning.

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# ANIMAL RELATIONSHIPS TO TRACE ELEMENT NUTRITION UNDER FLORIDA CONDITIONS

### R. W. KIDDER\*

The so-called trace elements have made a very important contribution to the success of all branches of Florida agriculture. As a result of this the public in general is perhaps more interested in these special elements and better informed about their importance than is characteristic of many other sections of the country.

Some regions are especially noted for their naturally healthy livestock. The Bluegrass region of Kentucky with its fine horses and the Shenandoah Valley of Virginia with its excellent cattle are typical examples of such areas. In these regions the major and trace elements are supplied by the natural soil in such proportions that there are no deficiencies or toxicities which appear in the livestock as an improper mineral balance.

In Florida there are areas of deficiency of both major (2) \*\* and trace elements as well as some places where toxicity is found. due to excess of some of the latter. Even though phosphorus mining is a major industry in Florida, some native pastures are deficient in this element (4) (18) (20). In such areas cattle consume all of the skeletons from dead animals and often chew up every piece of wood or lumber brought into the pasture from some other place. In other areas the cattle often chew oyster shells or other calcareous rocks indicating a craving for lime or calcium (5). Dairy cattle or beef cows nursing calves show these effects of lime deficiency more quickly than dry cows or steers, due to calcium being secreted in the milk. This secretion ocassionally is accomplished by the removal of calcium from the bones causing them to become thin and brittle and easily broken. Frequently trace element deficiencies appear in herds also deficient in phosphorus and calcium (3).

Inadequate nutrient diets especially during the winter months are often associated with trace element deficiencies. Minerals are essential to such animals but are not a substitute for total digestible nutrients nor for unbalanced rations due to lack of protein.

Florida cattle suffering from mineral deficiencies are often seriously handicapped by parasitic infestation. Under such conditions the animal fails to respond to worm treatment alone or to minerals but must have both conditions corrected to attain normal growth or production. Since some internal parasites are harbored by most Florida cattle and since clinical cases of para-

\*\*-Reference is to Literature Cited at end of paper.

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sitism are not common in cattle on adequate rations, the best control for internal parasites is to be sure the animal has an adequate ration, including digestible nutrients and minerals.

The natural feed for cattle is pasture grass. Cattle should be able to get all of their requirements of feed and trace elements from the pasture, if supplied with some salt, calcium and phosphorus. Before it was known how much copper cattle required in the Everglades, the cattle were maintained by feeding cotton-seed meal. Trace element problems can be handled by shipping in Prairie hay or other feeds to feed the cattle during the winter. Some cases have been observed where trace element problems were intensified due to the molybdenum content of alfalfa hay shipped into Florida.

The most common and satisfactory method of getting trace elements to Florida cattle is the mineral mixture box (2). The salt requirement of Florida cattle is less than that amount usually considered to be normal. When mixed with bone meal the salt acts as a preservative for the bone meal and the bone meal dilutes the salt making the combination more palatable than either one alone. The trace elements can be added readily to this combi-

nation.

To increase the palatability of mineral mixtures some have added feeds such as cottonseed meal, corn meal or molasses. A few very satisfactory mineralized pellets have been produced and used.

The cattleman must see that the minerals are kept dry in the box; that they are kept fresh by frequent refills; and that the height of the box is such that all animals can reach them

easily.

A satisfactory mineral mixture must be made available at a reasonable price. To keep the cost of the mineral mix at a minimum there should be included only those materials known to be lacking in the feed and these in adequate but not excessive amounts. A commercial concern should not attempt to sell a cattleman any mixture that does not meet the needs of the cattle in the area, nor one that contains some inert, unnecessary, or even harmful material in order to reduce its selling price.

One of the complications of understanding mineral mixtures is the difference between the registration tag and the percentage of each material included in the mixture. Many cattlemen read the list of elements included on the tag but do not understand the meaning of the figures representing the guaranteed analysis. When copper sulfate, for instance, is used as the copper source, each one percent copper sulfate adds 0.25 percent of copper element. This allows some dealer representatives to sell mixtures containing the correct elements but in quantities which do not meet the needs of the animals in certain areas.

The several trace elements necessary for Florida cattle are used by the animal in one or more ways. There may be a simple deficiency to be met. The particular element may be a necessary

catalyst in the assimilation of other necessary elements. There is strong evidence that some, such as cobalt, may be involved in supplying necessary nutrients for essential digestive flora. In the case of copper and molybdenum, the higher rates of copper are necessary to a large extent to counteract the toxic effect of excessive molybdenum, found in some forages. Experiments have not successfully differentiated between the symptoms of copper deficiency and those of molybdenum toxicity. Some areas have been found to be copper deficient where molybdenum has not been demonstrated in amounts known to be toxic. Cattle in these areas respond to high rates of copper consumption in the absence of toxic levels of molybdenum. Several years ago a few cattle from the Moore Haven area responded to aluminum (13). Most of the cattlemen in that area continue to use aluminum in their salt mixtures.

Iron in the form of red oxide has been used as a constituent of the mineral mixture fed Florida cattle for a number of years. Some areas may need this iron while other areas have adequate iron in their forage and drinking water. It is possible that part of the response to the 25 percent red oxide used in the salt mixture was due in some areas to the presence of other elements in the red oxide, such as cobalt and aluminum. The red oxide of iron contained nearly 3 percent aluminum.

The inter-relation and inter-dependence of these trace elements is important as well as the compound from which the element is derived. Experiments with copper illustrate the importance of knowing the relative effects of different compounds. A solution of copper chloride containing 10 mg. copper per 10 ml. water using the 10 ml. dose intravenously at 10-day intervals successfully cured advanced cases of copper deficiency. Copper sulfate (CuSO<sub>4</sub>.5H<sub>2</sub>O) given orally in 5-gram doses at 10-day intervals will correct copper deficiency. Copper oxide and basic copper sulfate will also correct copper deficiency when administered at the same copper level as contained in 5 grams copper sulfate. Metallic copper is now under trial and another copper product called "copper cement" will be tried later.

Soil treatments with copper sulfate at the rate of 100 pounds per acre produced grass which readily corrected copper deficiency for about two years, after which this curative effect was lost. This illustrates the futility from an economic standpoint of attempting to alleviate the trace element deficiencies entirely through soil amendments, at least under certain conditions.

Some cattlemen have dusted their pastures with copper sulfate by plane using 10 to 20 pounds per acre. Cattle grazing this grass get a large but uncertain dose of copper. Other cattlemen have added copper to the drinking water. It usually is possible to separate from the herd a few individual animals that require special attention and treatment with trace elements.

The extent or limits of copper deficiency in Florida are not well defined (21). Regions of greatest need are the muck areas



Figure 1.—Grade Devon heifer (EES. No. 129) at about 6 months of age showing early symptoms of typical copper deficiency, i.e. swollen ankles front and back, rough hair coat and uncomfortable posture even before scouring bleaching of hair coat or much loss of condition has occurred.

but copper deficiency is prevalent in most of the east coast areas from Palm Beach County southward. Cattle in the Arcadia area respond to extra copper. Many of the cattle from LaBelle southward show copper deficiency symptoms sometimes excessively under uncontrolled conditions.

Under certain conditions copper sulfate is toxic. One 500 pound steer was destroyed by chronic copper toxicity after 122 daily doses of 5 grams copper sulfate (14). The same amount of copper as copper oxide was administered to 2 steers daily for 15 months without developing any symptoms of toxicity.

Molybdenum toxicity has been mentioned as being similar to if not identical with copper deficiency. The other trace elements which may be toxic under certain conditions are cobalt and fluorine (6). Rare cases of over dosage with cobalt have been reported. An animal might have to consume 20 times its requirement to produce any undesirable effects. Fluorine is present in raw rock phosphate in sufficient amounts to severely affect the teeth of cattle. Defluorinated phosphate is used safely in mineral mixtures when prepared so that the fluorine content is less than 0.2 percent.

Several elements have been fed experimentally to Florida cattle without obtaining beneficial results. Arsenic was thus tried orally as sodium arsenate and intravenously as sodium cacodylate. A slight stimulation was the only measurable effect on the animals. Neither potassium as saltpeter or phosphorus as sodium phosphate were effective in improving the condition





Figure 2.—ABOVE: Devon calf (EES. No. 547) with congenital copper deficiency shown by stiff bent ankles, most severe in front. Note appearance of severe pain while trying to move. Photo taken before copper therapy was started.

BELOW: Same calf as shown above after having received 4 weeks of copper therapy which involved drenching with 1/10 gram of copper sulfate in 6 oz. water twice a week. As a result of this treatment this calf developed into a mature cow normal in every respect.



Figure 3.—Scapula of steer showing typical symptoms of copper deficiency locally known (Florida) as "Pacing." Note advanced disintegration of periosteum and even the bone structure in the darkening and darkened areas, respectively. A second steer showing the same condition which was slaughtered at the same time showed identical bone symptoms. Two other steers, which were similarly crippled at the same time, recovered fully as a result of proper copper therapy.

of cattle suffering from what is now known to be primary copper deficiency.

Symptoms of trace element deficiencies are generally similar regardless of which elements are lacking. With cobalt deficiency the animal suffers from anorexia (loss of appetite). With copper deficiency this symptom is absent and some animals develop the pacing gait, caused by inflamation of the periosteum of the scapula and the interior of joints in the legs.

Cobalt is a deficiency element on sandy soils more than it is on muck soils, consequently more cattle in Florida suffer from this deficiency than any other trace element (17).

There are some indications that other trace elements should be given to Florida cattle besides cobalt, copper, and iron. Consideration must be given for needs of aluminum, magnesium, zinc, manganese, and perhaps boron as well as some others. Some of these may be in the bone meal and, therefore, included in the mixtures being used.

To make a salt mixture which will meet the needs of cattle in all parts of Florida may not be possible or practical. Such a mixture should contain enough of each trace element to correct the deficiencies but not enough to create hazards of toxicity. This must be based on records of rates of consumption and the actual requirements of the animals as determined by careful test.

A mixture containing the following amounts has some ad-

vantages in much of Florida particularly in the southern part of the peninsula:

50 pounds steamed bone meal

45 pounds salt

2 pounds copper sulfate 1 pound copper oxide

2 pounds aluminum sulfate

1 ounce cobalt carbonate

The analysis tag for this mixture would read:

Calcium (Ca) 13.00 percent
Phosphorus (P) 6.00 percent
Salt (NaCl) 45.00 percent
Copper (Cu) 1.27 percent
Aluminum (Al) .20 percent
Cobalt (Co) .03 percent

Some might want to add iron to this mixture. Perhaps the cost could be reduced if part of the calcium and phosphorus came from the defluorinated phosphate. These additions, however, would reduce the palatability and consumption rates.

As this formula stands there is no danger of copper toxicity because three-fifths of the copper is from oxide and two-fifths from sulfate. Only the sulfate is toxic and 0.5 percent of copper (Cu) from this source is well within the limits of tolerance. If the animal needs more than that amount the 0.75 percent from the non-toxic source of copper oxide is available without danger of injuring the animal.

The highest rate of consumption on our records for approximately this formula is 40 pounds per animal annually. At 1.25 percent elemental copper this is an annual consumption of 0.5 pounds of the element. This is equivalent to about 3 grams CuSO<sub>4</sub> average daily intake for one year. The animals consuming

this amount remained normal in every way.

Continuing research probably will indicate that cattle need other trace elements. Manganese is one which has been studied However, sufficiently definite results were not obtained to indicate that it should be included. While these studies are being continued a mineral mixture similar to the one given should keep the cattle of Florida in reasonably good health.

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# SOME ESTIMATES ON THE AMOUNTS OF SECONDARY PLANT FOODS USED ON FLORIDA CROPS

## J. J. TAYLOR\*

An attempt has been made to determine as closely as possible the approximate amount of secondary plant foods used in Florida agriculture during the past year. Several manufacturers were requested to furnish us information as to the tonnage used in their manufacturing of mixed fertilizers on the following items: copper, manganese, zinc, boron, iron and magnesium.

The several manufacturers who sent us reports gave a total tonnage of magnesium in its various forms as 15,943 tons. Since magnesium was by far the largest single item, it may be of interest to show that of this total 13,755 tons were sulphate of potash with magnesia, 1,335 tons of magnesium sulphate (Emjeo) and a small tonnage of seawater magnesium oxide, magnecite and brucite. This does not include dolomite.

Other secondaries were Copper sulphate 1,641 tons, Manganese sulphate 2,654 tons, Zinc sulphate 326 tons, Iron sulphate 496 tons, Borax 288 tons, making a total tonnage of secondary plant foods of 21,348 tons. The companies which reported these figures to us put out a combined tonnage of approximately one-third of the total tonnage of the State.

Assuming that the other manufacturers of the State used secondary plant foods in their mixtures in approximately the same proportion as those reporting, it would indicate that between 60 and 65 thousand tons of secondary plant foods are going into mixed fertilizers each year in Florida.

<sup>\*—</sup>State Chemist, Chemical Division, State Department of Agriculture, Tallahassee, Florida. This communication was in the form of a letter to the Secretary of the Society.

# THE RELATIONSHIP OF TRACE ELEMENTS TO THE GROWTH OF AGRICULTURAL PLANTS IN THE WESTERN STATES

FRANK E. GARDNER\*

In view of the fact that the time of our meetings in June conflicted with certain National and International meetings in both plant and animal sciences it was not found possible to have a representative from the West Coast either prepare a paper on the above subject or be present in person for its discussion. In consequence of such a situation, Dr. Gardner very kindly agreed, on very short notice, to give a purely extemporaneous review of the work that has been done out there and is under way at the present time. This he was able to do very well indeed because of his personal responsibility for the USDA Sub-tropical Fruit Program in California and Florida, with headquarters at Orlando, and because of his quite intimate knowledge of past accomplishments and present activities in the field of plant physiology in both sections of the country.

In his brief review, Dr. Gardner of course dwelt at some length on basic work in plant nutrition that has been done in the west during the past quarter century by an extensive sequence of brilliant workers stemming from the time of Dr. C. B. Lipman and his contemporaries and also covered many of the practical applications of this work in the field where it has done so much for culture of such perennials as citrus, walnuts and olives as well as many other horticultural crops and farm crops. Ed.

<sup>\*-</sup>Principal Horticulturist in charge of Sub-tropical Fruit Investigation, U.S.D.A., Orlando.

# REGIONAL REPORT ON TRACE ELEMENTS IN PLANTS AND SOIL IN THE NORTH CENTRAL STATES

### ROBERT E. LUCAS\*

Before discussing trace element studies for the North Central States, I must state that our work is behind the research here in Florida. Much of our findings are no more than facts confirming your observations.

Only in the last decade have we realized the extensive need for the major plant nutrients, N-P-K. When I was attending Purdue during the late '30's, we were instructed that properly fertilized corn should get 75-150 pounds per acre of O-14-7, and wheat 150-200 pounds per acre of 2-12-6. What a change has come about both in the amounts and in the formulaes! It is no wonder that trace element research has been neglected. Now that crop specialists have major nutrient problems reasonably evaluated, they are beginning to broaden their interest and include trace element studies. From the investigations already made, we are finding that not only may a lack of certain trace elements affect crop yields, but it may also cause malnutrition in animals. Another reason for our neglect in trace element research is the difficult task of determining the amounts present in plant material and in the soil. The use of new spectrographic techniques and the colorimetric methods are overcoming this quantitative problem.

Of the states in our area, Michigan has probably contributed the most research in trace elements. According to Dr. J. F. Davis,\*\* members of the Michigan State College Soil Science Department have published over 50 papers and reports on this subject. At the present time nearly 40 crops are listed as needing trace element fertilization. Many of these recommendations deal with crops grown on muck soil. The organic soils in Michigan amount to approximately five million acres. Of this acreage only a small part is now under cultivation. However, that under cultivation often needs one or more trace elements for maximum crop growth. On the mineral soils, alfalfa, beans, and sugar beets often need trace element fertilization. There are large

acreages of these crops in Michigan.

Dr. K. C. Berger\*\* informs me that the consumption of trace elements in Wisconsin is constantly increasing. This is particularly true of borax. He believes that nearly two-thirds of the acreage in alfalfa shows boron deficiency. In 1949 over 1000 tons of borax were used. The use of other trace elements has not been as spectacular but they have a need for manganese on

<sup>\*—</sup>Agronomist in charge of research, Wm. Gehring, Inc., Rensselaer, Ind. \*\*—Private communication.

the alkaline (calcareous) soils, particularly for oats and wheat.

Dr. Ohlrogge,\* reporting for the Purdue Agronomy Department, stated that about one-fourth of their fertility funds are for minor element studies. He felt the proportion was a fair balance with other fertility problems, and he did not expect much

of a change in the near future.

In general the trace elements which give us the most trouble are boron and manganese. Both elements are usually deficient on over-limed and calcareous soils. Boron deficiency is corrected by mixing borax in the fertilizer at the rate of 10-25 pounds per acre. Because the amounts are small and the material inexpensive boron may soon be a standard recommendation for all alfalfa and beet fertilizers. Manganese deficiency is corrected either by applying as a fertilizer (50-100 pounds per acre of manganese sulfate) or as a spray (3-10 pounds per acre). The use of sulfur and acid forming fertilizers may be recommended by some crop specialists.

Recently the need for copper is being recognized on soils other than organic soils. Berger reports that sweet corn responds to this element when grown on some Wisconsin sandy soils. In 1949 our organization lost about 50 acres of wheat because of a severe copper deficiency. The soil type was a Newton sandy loam. This wheat followed a good potato crop. If we would have used Bordeaux instead of Dithane as the fungicide for potatoes we would not have observed the trouble in the wheat. Incidentally, test spray plots on the wheat foliage showed that molybdenum stimu-

lated growth as well as copper.

The use of zinc as a fertilizer is not common in our area for seldom does one see zinc deficiency symptoms on crops; nevertheless, the use of zinc fertilizers and sprays does improve the yield and quality of produce. We are observing the benefits of zinc more since we have been using it in our fungicide sprays. The findings of Hoyman in North Dakota on potatoes well illus-

trates plant stimulation due to zinc sprays.

In the past our work with trace elements has been mostly field experiments, describing deficiency symptoms, and correlating soil factors which cause trace element problems. Such studies are fundamental, but they do not answer the role of trace elements in plants. We have practically no information on what effect trace elements have on the animals that consume feeds which contain various amounts of trace elements. The inter-relationship of trace elements in plants is also a field which needs greater study.

Using trace elements in our fertilizer is causing some manufacturing problems. One is the tendency to express the amount in fertilizer as the per cent carrier in the fertilizer rather than as the elemental form. Another problem is, how are we to label the bag for N-P-K when trace elements are added? Most states require that the manufacturer adhere strictly to the rule in that

<sup>\*-</sup>Private communication.

they sell only recommended formulaes and that the analysis be correct on a percentage basis. Since the proportions and the calls for trace elements are so variable, the fertilizer companies find it difficult to meet recommended formulaes and still keep down production costs. Recognizing this problem, the Michigan muck farmers have asked their state chemist to permit the sale of standard grade fertilizers that have trace elements added when requested. For example, if a farmer wants 100 pounds per ton of copper sulfate in his 0-10-20, then the company makes a mixture of 1900 pounds of 0-10-20 and 100 pounds of copper sulfate. An additional tag is then placed on the bag showing the correct formulation. Our organization used about 500 tons of fertilizer with trace elements added. We believe the system used by the Michigan people is clear and simple and helps keep down production costs.

The Wisconsin fertilizer people are trying to follow the system of mixing trace elements in high analysis grades and then selling the fertilizer as a medium grade. For example, 3-12-12 with trace elements is made from 5-16-16; 0-9-27, containing borax is made from 0-10-30.

Another question which often comes up is whether we should buy "mineralized" fertilizers (those containing all known trace elements) or fertilizer with only the requested trace elements added. Either practice has its good points. "Mineralized" fertilizers have paid returns on some crops because we failed to recognize the various trace element problems. On the other hand, such fertilizers are more expensive and one may be buying ingredients which are not necessary. Furthermore, certain crops like beets and alfalfa require quantities of boron which would prove disastrous for beans and small grasses. The same problem might be true for copper and manganese. According to Berger the inclusion of manganese in fertilizer would injure potatoes growing in parts of Wisconsin. In general, I feel that as we become more informed in trace elements, we will use them only for certain crops and soil types.

Our workers have recently become interested in the effect of trace elements upon quality. Those familiar with boron physiology know that a lack of this element in such crops as celery, beets, alfalfa, and turnips can markedly lower quality. Some of my study in trace elements has been to determine the effect of copper fertilization on the ascorbic acid and carotene content of plants. It was found that there was no effect in some crops while others showed definitely significant differences. The protein content of copper deficient plants was found to be high. Sherman and Harmer (Michigan) have shown that manganese deficiency may lower the ascorbic acid in plants. The sugar content of carrots and table beets was also found low when these

crops were grown on copper deficient soils.

A series of 5 photographs is appended to show some of the plant responses that have been referred to above.



Figure 1.—Corn showing copper deficiency growing on acid muck in Indiana. Symptoms—yellow streaks on leaves. Top leaves may be solid yellow. Distinguished from zinc deficiency by absence of any white areas.



Figure 2.—Corn showing zinc deficiency growing on Newton sandy loam, Jasper County, Indiana. Symptoms—same as described for zinc deficiency of corn in Florida—characteristic white bud area. In advanced stages the lower leaves show purple color.



Figure 3.—Oats showing copper deficiency growing on muck soil in the greenhouse. Symptoms—light yellow cast to leaves with some streaking. Top young leaves show more yellow than older leaves and may fail to open from curl. Slight tip dying. Note: Deficiency symptoms of wheat show pronounced lemon yellow color. Distinguished from nitrogen and manganese deficiency by high nitrate nitrogen test and a noticeable dying at the end of the leaves.



Figure 4.—Check row in soybean field that had not been sprayed with manganese sulfate. This trace element problem is common in over-limed soils of Northern Indiana. Symptoms—lemon yellow to nearly white leaf color, especially on young leaves. Slightly affected leaves show prominent, dark colored veins. Photo courtesy of the Agronomy Department, Purdue University.



Figure 5.—Marked effect of soil fumigation with Dichloro-propene (Dow Fume N) on the growth of wheat. Light area on left not fumigated; dark colored plants on right fumigated. The actual response was a correction of manganese deficiency.

# TRACE ELEMENT RESEARCH IN THE NORTH EASTERN STATES

### E. R. Purvis\*

According to a recent survey (1), 12 trace elements have been investigated by the various Experiment Stations of the northeastern states. Beneficial results have been obtained from field applications of salts of boron, copper, iron, manganese, molybdenum and zinc to certain crops. To date, negative results have been obtained from plant studies with cadmium, chromium, cobalt, iodine, strontium and vanadium. Forage plants have been found to contain insufficient cobalt to meet animal requirements in some areas of New Hampshire, New York, Massachusetts, and Vermont.

#### Boron

Boron is the trace element most commonly found to be deficient in the soils of this region and alfalfa the crop most widely affected. Apples have responded to applied borax in Connecticut, New Hampshire, New York, Rhode Island, Vermont and West Virginia. Beets, broccoli, cabbage, cauliflower, celery, Ladino clover, tomatoes, and turnips are other crops often found to suffer from insufficient boron. A small increase in the yield of potatoes due to applied borax has been reported from Pennsylvania.

It is likely that most of the soils of the northeastern states are deficient in available boron—at least during certain periods of the year—for the growth of crops having a high requirement for this element. During the dry summer of 1949, boron deficiency was observed for the first time in alfalfa growing on some of the heavier soil types in Northern New Jersey. Prior to this time, these soils had been thought to contain sufficient available boron for normal growth of alfalfa. Similar reports of the effect of drouth in producing boron deficiency have come from Connecticut. The Storrs Station reports that they have yet to test a Connecticut soil by the pot-culture method and find sufficient boron for the normal growth of turnips.

All states of the northeast recommend borax for alfalfa when grown on soils known, or suspected, to be deficient in boron. These recommendations vary from 20 pounds of borax per acre annually to 40 pounds applied once in the alfalfa rotation. The borax is usually mixed and applied with fertilizer. Such applications have become so common that most fertilizer companies operating in the area offer standard mixtures containing borax for alfalfa. In the 6 states where boron deficiency in apples

<sup>\*—</sup>Prof. of Soils and Research Specialist in Soils, N. J. Agr. Expt. Station, New Brunswick, N. J.

has been identified, from 2 to 8 ounces of borax per tree, depending upon tree size, is recommended. Such applications are repeated every 2 or 3 years. Recommendations for vegetable crops vary from 10 to 40 pounds of borax per acre, depending upon the crop and soil type. New Jersey recommends that all fertilizers contain 5 pounds of borax per ton and that fertilizer for tomatoes contain sufficient borax to supply 10 pounds to the acre.

Most state laboratories in the Northeast test soils for available boron. In New Jersey, 0.35 parts per million of available boron is considered the critical level below which crops are likely to respond to applied borax. Plant tests and the identification of deficiency symptoms are other methods employed for

detecting boron-deficient soils.

# Manganese

Manganese deficiency is probably the second most important trace-element problem of this area. Deficiencies of this nutrient have been reported on overlimed soils only. In most instances the pH of deficient soils exceed 6.5, although deficiency may occur at a slightly lower pH on light sandy soils. Vegetable crops, such as beans, beets, cabbage, cauliflower, and spinach, are commonly affected. There are instances, however, where the deficiency has been reported in alfalfa, apples, clover, corn, peaches, and the small grains.

Recommendations for the correction of manganese deficiency include soil treatment with manganese sulfate at the rate of 50 to 100 pounds per acre or spraying of crops with a dilute solution of manganese sulfate. In other instances the application of sul-

fur to reduce the soil pH is resorted to.

Manganese toxicity on acid soils has been reported in apples in West Virginia, tobacco in Connecticut, and in several limeloving crops in Pennsylvania. Results from a study of the mineral composition of leaves from a large group of native plants in the latter State show that one of the chief differences between calciphile and calcifuge plants lies in their manganese content.

# Copper

Copper deficiency in the Northeast is believed to be confined to organic soils and is most likely to occur during the first few years that such soils are cultivated. The deficiency probably affects all crops but is usually reported in vegetable crops since the peat areas of this section are normally planted to such crops. In New York, the thickness and color of the scale of onions were improved by applications of copper sulfate up to 300 pounds to the acre. Connecticut studies have indicated that applied copper may counteract manganese toxicity in alfalfa.

## Iron

Iron deficiency rarely occurs on the normally acid soils of

the Northeast. The deficiency does appear, however, when some soils are overlimed. Iron deficiency has been reported in vegetable crops growing on Connecticut soils that received heavy applications of wood ashes. New York reports the deficiency in blueberries and in most tree fruits grown in high-lime spots. Spraying with a 1 per cent solution of ferrous ammonium sulfate is recommended for deficient blueberries. In New Jersey, the injection of iron salts into the trunks of affected trees is recommended for correcting iron deficiency in pin oaks.

## Zinc

Response to applied salts of zinc have been reported with potatoes in Maine and with corn in Maryland. Great variation has been found in the available zinc content of New Jersey soils and recently zinc deficiency in apples and peaches has been reported in this State.

# Molybdenum

Considerable work with molybdenum has been done in New Jersey during the past 2 years. The total molybdenum content of samples from 18 important New Jersey soils was found to vary between 0.8 and 3.3 parts per million. Alfalfa from a number of locations was found to contain from less than 0.1 to 1.4 parts per million of molybdenum on the dry-weight basis.

Significant increases in yield have been obtained from applications of 1 pound sodium molybdate per acre in 5 out of 6 field tests with alfalfa growing on some of the heavier soil types. These increases ranged as high as 27 per cent and averaged 13 per cent for all tests. The molybdenum-treated alfalfa was found to contain appreciably more nitrogen than untreated plants in

4 of the 6 tests.

Results from greenhouse pot tests indicate that one of the principal benefits of liming upon the growth of alfalfa may lie in the release of molybdenum from the soil. Working on the theory that plants grown on acid soils may have difficulty in obtaining sufficient molybdenum, a remarkable response was obtained in a greenhouse test in which potato seed pieces were dipped in an 0.10% solution of sodium molybdate. An increase in tuber production of 87% was obtained. This treatment is being tested in the field at 6 locations in New Jersey this season.

Recently the New York Station has reported that molybdenum teatment eliminated "whiptail" in cauliflower when applied to acid Long Island potato soil in a greenhouse test.

# Current Trace-Element Research in the Northeast

Interest in trace-element research continues in all States of the Northeast. Most of the agricultural experiment stations of



Figure 1.—Response of Katahden potato to treatment of seed piece with molybdenum shown growing under greenhouse conditions in a Nixon sandy loam with a pH of 5.2 and a uniform treatment with NPK. Photo taken 107 days after planting.

LEFT—no treatment of seed piece. RIGHT—seed piece dipped for 10 minutes in a 0.01 percent solution of sodium molybdate.

the area have active projects underway at present. The nature of these projects vary from surveys to find deficient areas to elaborate projects involving the work of a number of investigators. Projects of the latter type are under way in Connecticut, New York, and New Jersey. In the latter state, the soil and plant status of copper, cobalt, chlorine, fluorine, iodine, manganese, molybdenum, and zinc are each being investigated in one

or more projects.

The physiological relationships existing between the various trace elements in plant nutrition are attracting more and more attention. The effect of copper in partially correcting manganese toxicity has been mentioned. There is evidence that the molybdenum requirement of legumes is increased on soils having a high available manganese content. Molybdenum salts have been found to partially counteract the toxic effects of heavy applications of borax to alfalfa. The relationship between the roles of iron and manganese in plants remains a controversial issue. The

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importance of trace elements in the formation and activity of plant enzymes is being more widely recognized. All of these factors indicate that the blind application of trace-element mixtures on a "cure-all" basis should be viewed with caution. Such treatment may well create problems of a more serious nature than those it was intended to correct.

#### REFERENCES

1. Correspondence with staff members of the various Experiment Stations of the Northeast.

# PLANT RESPONSE TO TRACE ELEMENTS IN SOUTHEASTERN UNITED STATES

### JAMES A. NAFTEL<sup>1</sup>

Soils, climate and crops of the South are such that trace elements are important in crop production. Large areas of the South consist of sandy or light textured soils, easily leached and with low organic matter content. The climate is characterized by relatively high temperature and rainfall. Crops grown include field, vegetable, fruit and tree crops, as well as many ornamentals.

During the past 75 to 100 years most of the crop land has been clean cultivated, thus exposing the soils to the extreme ravages of erosion, oxidation and other processes of soil nutrient losses. Many of the soils have been formed under conditions of extreme weathering and hence losses of much of their mineral

content.

Recently through educational, economic, and governmental programs, large acreages of row crop land are being diverted to sod crops or what is now commonly referred to as "Grassland Farming." This trend toward sod crops will have significant effects on the needs and conservation of trace element plant nutrients since this development includes many leguminous plants

that respond favorably to some trace elements.

Soil fertility investigations were begun at some experiment stations in the South more than 50 years ago. Major interest was in N.P.K. and lime during that time, which resulted in the well-known use of commercial fertilizers. Of the approximately 10 million tons used in the 13 Southeastern States in 1949, North Carolina alone used more than 1.8 million tons. The use of lime has not kept in balance with the use of the major elements; in large areas too little lime has been applied while in others exces-

sive amounts have been used with unfavorable results.

Trace element studies in the South had their beginning about 25 years ago when it was found that certain observed abnormalities of crops were not avoided despite the use of the commonly used major plant foods and lime. Actually the first experience of the author was in the Florida Everglades during 1926-28 in connection with Cu deficiencies on peanuts. Reports on the early trace element studies were made by Allison, Bryan, and Hunter in 1927. Interest and investigations of trace element needs followed a natural development in the field of soil fertility and plant nutrition in that chemical methods and technique had to be developed not only for detecting and estimating the content of B, Cu, Fe, Mn, Mo, Zn, etc., but also to prepare pure culture mediums for fundamental studies. From this beginning of trace element

<sup>1—</sup>Agronomist, Pacific Coast Borax Co., Auburn, Alabama.
2—Allison, R. V., Bryan, O. C., and Hunter, J. H. Florida Agricultural Experiment Station Bulletin, No. 190 (1927).

studies in Florida, investigators in Alabama, Georgia, Kentucky, North Carolina, and Virginia reported on early investigations

during the middle and late thirties.

Trace element studies in the Southern United States during the last two decades have in the main been in applied rather than in pure science in an effort to determine plant response to additions of single or combinations of trace element compounds to soils. Trace elements have been supplied to crops and soils by applications in the regular fertilizer mixtures or as direct applications in dusts or sprays singly or in combination with pesticides. Where there are specific recommendations for the use of trace elements for certain crops, the fertilizer manufacturer can incoporate the trace element into the fertilizer mixtures with a guarantee of analysis. Also where there is a general recommendation for the incorporation of minimum amounts of trace elements in all grades of fertilizers within a state, as some are now doing, the fertilizer manufacturer has no particular problem in compliance. The real difficulty in supplying trace elements is where prescription and varying amounts are requested by growers. There is an increasing interest in foliar application of trace elements, especially on fruit and vegetable crops where sprays and dusts for pest control are a matter of routine practice. The latter application can be made without much additional cost.

The present discussion, therefore, will be largely concerned with the response of crops to trace elements in the Southeastern United States. For convenience the trace elements, B, Cu, Fe, Mn, Mo., and Zn, are arranged alphabetically and will be dis-

cussed in this order.

Boron:—Soil contents of B in the Southeast vary from ample amounts in the heavier more fertile soils to deficient amounts in the light sandy types of soil. B deficiency may be induced by over-

liming on some soils.3

Alfalfa has been one of the most valuable farm crops in large areas of the country but was generally found to be unsuccessful in the Coastal Plains and areas of other sandy type soils of the Southeast until B was added in addition to lime and other fertilizers. Now every state in the Southeast is producing alfalfa crops of from 3 to 5 tons of hay annually and using from 10 to 40 pounds of borax equivalent per acre in the regular fertilizer mixtures.

Other field crops on which favorable practical results have been obtained with B fertilization are crimson, bur, button, red, and white clover, sweet corn, sweet potatoes, and tobacco, the latter crop responding favorably to only  $2\frac{1}{2}$  lbs. borax per acre.

Boron has been commonly used on many truck crops in the

4-Willis, L. G. and Piland, J. R.; A Response of Alfalfa to Borax, J.

Amer. Soc. Agron. 30: 63-67 (1938).

<sup>3—</sup>Naftel, James A.; Soil Liming Investigations: V. The Relation of Boron Deficiency to Overliming Injury, J. Amer. Soc. Agron. 29: 761-771 (1937).

Southeast since the early report of Purvis and Ruprecht<sup>5</sup> of the need for B addition to celery. Other vegetable crops quite commonly fertilized with B are beets, broccoli, cabbage, carrots, cauliflower, lettuce, radishes, rutabagas, tomatoes, and turnips. Generally boron at the rate of 10 lbs. borax equivalent per acre has been recommended for the vegetable crops, although the more recent investigations have shown favorable results with lower rates of boron such as 5 lbs. borax equivalent per acre.

Fruit crops in the Southeast that respond to boron are apples, citrus, and grapes. Boron deficiencies are corrected on apples by applying from  $\frac{1}{3}$  to 1 lb. of borax equivalent per tree as a direct application or with the other fertilizers. Where B deficiency has been noted on citrus in Florida, boron is supplied to trees either in the spray or fertilizer applications. Foliar and fruit symptoms of B deficiency on grapes were corrected in South Carolina vine-

yards by applications of 10 pounds of borax per acre.6

Copper:—Cu has been noted to be deficient in peat, muck, and other highly organic soils on the one hand and on sandy soils on the other extreme. Furthermore, organic and heavy soil types require and withstand more Cu than light soils. Due to the widespread use of sprays and dusts which contain Cu. there have been few clearcut examples of Cu deficiencies reported on crops grown in the field with the exception of those reported in Florida and in small areas of organic soils that contain high contents of lime.

Iron:—This element becomes a problem in plant nutrition on calcareous or alkaline soils. On some soils such as Sumter clay, which occurs in the black belt area of Alabama, Mississippi, and Texas, peanuts, common lespedeza, crimson clover and some grasses fail to make satisfactory growth due to iron deficiency. Soil applications of iron do not correct the deficiency but spray applications of iron compounds have given favorable results on experimental plots. On the other hand, small grains and Johnston grass appear to obtain sufficient iron on the above soil.

Iron deficiency has been recognized on citrus in Florida for a number of years but this is being covered in another report.

Ornamentals such as azaleas, camellias, roses, etc. often show iron deficiency when grown in soils with relatively high pH values; these deficiencies may be corrected either by spray application or by adjustment of soil reaction.

Manganese:—Soil acidity is one of the most important factors influencing the availability of Mn to plants. The strongly acid, sandy soils of the Southeast are most likely to be low in Mn, and when such soils are excessively limed, Mn deficiency may occur. The brown, chocolate and red soils often contain

<sup>5—</sup>Purvis, E. R. and Ruprecht, R. W.; Cracked Stem of Celery Caused by a Boron Deficiency in the Soil, Fla. Agri. Exp. Sta. Bul. 307 (1937).
6—Scott, L. E.; The Effect of Boron on Fruit Production, S. C. Exp. Sta. 54th Annual Rept.: 151-155 (1941).

high contents of Mn. The latter soils may contain sufficient soluble Mn to be toxic to some crops when the soil acidity is high.

Cotton, corn, peanuts, small grains, soybeans, and tobacco have been observed with Mn deficiency symptoms in some field soils of the Southeast. Recent reports by Shear and Batten<sup>7</sup> of the Virginia Station have pointed out the need for Mn applications on corn and peanuts where lime has raised the soil reaction above pH 6.0. Increases of peanuts of as much as 400% have been obtained by proper application of manganese sulfate of about 20 lbs. per acre. Truck crops such as beets, cabbage, cucumbers, peppers, spinach, and tomatoes have shown Mn deficiencies in the eastern truck belt from southern Florida to Maryland.

Molybdenum:—Although Mo has recently been recognized as an essential element for plant growth and some field trials of added Mo have given yield increases of alfalfa and certain clovers, no results have been reported in the Southeast.

Zinc:—This is another essential plant food element that may be deficient in some soils especially where liming has been excessive on soils of low Zn content. Corn has been the field crop in the Southeast that most commonly responds favorably to Zn application. Corn on light textured soils, heavily fertilized and with a high plant population quite frequently shows "white bud" or Zn deficiency in the early stages unless Zn has been supplied with the regular fertilizers or as a direct application. As a result of field tests with corn in recent years, Zn is quite commonly added as a regular part of commercial fertilizers.

Tree crops such as pecans,<sup>8</sup> tung nuts and citrus have shown Zn deficiencies which are commonly referred to as "rosetting," "bronzing," or "frenching," respectively. Corrective additions on Zn either in the regular fertilizers or in the spray and dust

applications have proved practical remedies.

Application of Trace Elements to Plants:—The practical use of trace elements has received considerable attention in recent years, particularly is this true as to the most feasible methods of applications for correcting nutrient deficiencies. Direct application of trace element compounds to soils or crops in desired amounts either as single elements or in combinations of trace elements was formerly the general procedure. Now, some trace elements are applied for crops as a regular part of commercial fertilizer. More recently, trace elements have come into practical use as dusts or sprays on crops where the latter are regular parts of the crop management program. It may be expected in the

<sup>7—</sup>Shear, G. M. and Batten, E. T.; Manganese for Peanuts and Corn, Mimeographed series, Virginia Agrl. Exp. Sta. (1950).

<sup>8—</sup>Alben, A. C., Hammar, H. E., and Sitton, B. C.; Some Nutrient Deficiency Symptoms of the Pecan, Amer. Soc. Hort. Sci. Proc. 41:53-60 (1942).

future that more vegetable and fruit crops will receive their needed requirements of trace elements as a part of the pesticide application, thus avoiding some of the complications involved in soil reactions.

Problems Needing Study in Trace Element Research:—Future investigations on plant requirements of trace elements should include the following:

- 1. Interactions of one or more trace elements on the other.
- 2. Further studies on diagnostic techniques of trace elements.
- 3. Residual effects of trace elements applied to soils.
- 4. Efficient forms or sources of trace elements.
- 5. Optimum rates of applications of trace elements for the most efficient production of quality crops.
- 6. Improvement and calibration of soil and tissue methods of chemical analysis for trace elements.
- 7. Continued study of most efficient method of application of trace elements.

A series of 5 figures is appended to show some of the results that have been obtained thru the use of trace elements in the Southeast as referred to in the brief discussion above.

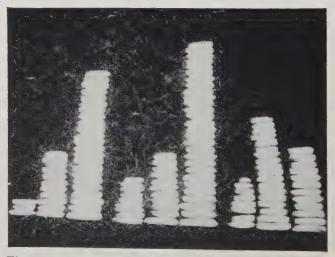


Figure 1.—Ears of sweet corn harvested from field plots in a boron experiment. The column of ears at the right in each category of treatment shows the relative yield of prime ears. Medium or imperfect ears are shown in the center and the nubs and immature ears are at the left. Fertility treatments uniform with the exception of boron. Photo courtesy Edisto Branch, S. Car. Agr. Expt. Station.

Treatment Right—no boron.
Treatment Center—5 pounds borax per acre.
Treatment Left—10 pounds borax per acre.



Figure 2.—Yield of No. 1 sweet potatoes from different applications of boron: Right, none; center, 5 pounds borax per acre and left, 10 pounds. The yield per acre of marketable potatoes for each treatment was 153, 235 and 186 bushels, respectively. Photo through the courtesy of the Edisto Branch, S. Car. Agr. Expt. Station.



Figure 3.—Effect of boron on the growth of cabbage in a limed soil under greenhouse conditions: LEFT—No boron. RIGHT—Boron treated.



Figure 4.—Boron deficiency in cauliflower growing in Baldwin County, Alabama, as shown by hollowness and "browning" in stem on left in comparison with sound, firm condition in that on the right. Photo courtesy of Alabama Agricultural Experiment Station.



Figure 5.—Response of alfalfa to treatment of a high lime soil with boron. LEFT—20 pounds of borax per acre. RIGHT—no treatment. Photo courtesy Alabama Experiment Station.

# EXCESS MOLYBDENUM IN FORAGE IN CERTAIN LOCALITIES IN CALIFORNIA\*

### HAROLD Goss\*\*

For many years, a cattle disease characterized by intense diarrhea, emaciation and change in coat color has been reported at intervals by ranchers on the southwestern edge of the San Joaquin Valley in central California. Much of this area is devoted to oil, livestock, alfalfa and cotton production. In recent years, cotton acreage has decreased and has been replaced by irrigated pastures. A number of different dairies are reported by the Farm Advisor's Office to have started between 1930 and 1940 in the affected area and failed because of this disease. Following Muir's (1) discovery in 1941 that the cause of scouring among cattle in the so-called "teart" pastures of Somerset, England, was due to an excess of molybdenum in the soil and forage, an investigation of the affected area in California by Britton and Goss (2) showed that plants in the pastures where excessive scouring occurred contained from 6 to 36 ppm. of molybdenum, while similar plants from normal pastures on the Davis Campus of the College of Agriculture contained only 0.5 to 1.5 ppm. molybdenum. Ferguson, et al. (3), and Muir (1) reported that teart pastures contained more than 14 ppm. while non-toxic pastures never contained more than 6 ppm.

Since our first report (2), a survey has been undertaken by W. P. Kelley and I. Barshad of the Division of Soils, of the occurrence of toxic quantities of molybdenum in pastures of that part of the state. The results of this survey, reported in part by Barshad (4) show the area affected to be much larger than susspected. Molybdenum contents as high as 193 ppm. were reported in some legumes from a newly planted irrigated pasture. A large number of suspected plant samples have been analyzed in the author's laboratory and we now have evidence which shows toxic levels of molybdenum in limited areas as far south as Death Valley Junction, one area to the west in Santa Barbara County. and as far north as Madera County. Samples of range grasses taken from various areas in the foothills of the Sierra Nevada have shown 3 to 6 ppm. which is not considered toxic. The highest concentration yet recorded, over 550 ppm., was found on the east side of the range in a section of Nevada.

Control of the molybdenum poisoning is being achieved by feeding copper sulfate to the cattle, either in salt or in the drinking water, in an amount which would bring the total copper con-

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sumed by the animal equivalent to 50 ppm. of the dry matter of

the forage.

Although we had received no reports that sheep were affected in the same way as cattle, we have demonstrated that high molydenum is toxic to sheep. We fed black sheep on a ration of barley and alfalfa hay to which was added sodium molybdate so that the total molybdenum concentration was 200 ppm. on the dry basis. Within 10 days to two weeks on this diet, the new wool over the whole of their bodies was observed to be coming in without the black pigment. After 15 weeks on this high level of molybdenum, there was a layer of grey wool 1 to 2 cm. thick on each of the black sheep. In a control experiment where the ration contained 200 ppm. molybdenum plus an addition of copper sulfate equal to 100 ppm. copper on the dry basis, there was normal pigmentation of the wool throughout the experimental period.

When 100 ppm. copper as copper sulfate was added to the experimental high molybdenum ration, the normal black pigmentation returned to the new wool fibers. These effects are illustrated in the photograph. Not only is the normal pigment absent in these "grey" wool fibers, but the physical properties are notably altered. J. F. Wilson is making a study of the affected wool fibers. No scouring of the sheep was noted in any of these

trials on dry roughage.

In experiments with black horses and pigs, black chickens and turkeys and black rats, no change in coat color of the animals, or feather color of the birds was noted on high molybdenum rations.

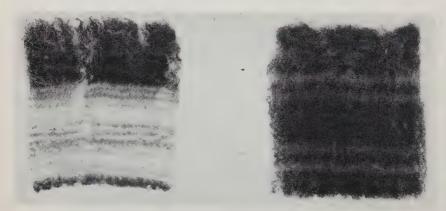


Figure 1.—Cross section taken from the fleece of a black sheep to show the effect of molybdenum feeding. LEFT—Layer of grey wool 1-2 centimeters thick which appeared as the new growth during a period of 15 weeks when the animal was fed on a ration of barley and alfalfa to which had been added sufficient sodium molybdate to give a total molybdenum concentration of 200 ppm. on the dry basis. RIGHT—Normal black wool profile also showing how the black pigmentation returned to the wool fibers upon adding 100 ppm. of copper as copper sulfate to the diet containing the high molybdenum.

The disorder produced by excess molybdenum seems to be specific for ruminants.

# Summary

The occurrence of excess concentrations of molybdenum in the soils of certain areas in California and Nevada has produced forage which is toxic to cattle. The toxicity is marked by excessive scouring and loss of coat color. In experimental feeding of black sheep on dry rations of high molybdenum concentrations. the new wool grows in without black pigment. No scouring was noted. Copper sulfate protects and restores the normal black pigment to the new wool and prevents the scouring and loss of coat color in cattle.

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# SOME TRACE ELEMENTS AND ANIMAL RELATIONSHIPS IN THE EASTERN AND SOUTHERN STATES

OF THE U.S. A.

GEORGE K. DAVIS\*

In this brief discussion of observations which have been made on trace elements and animal nutrition in the Eastern and Southern states, let me first list the states included.

Roughly the region is bounded by the Ohio and Mississippi Rivers to the West and the Atlantic Ocean on the East and extending North from the Gulf to the St. Lawrence. Including Ohio and Louisiana, there are 22 states in this area. As of this time experimental investigations of trace element deficiencies in domestic animals have been carried on in less than 10 of these states. Intensive studies have been made in New York, North Carolina, New Hampshire, and Ohio. On the other hand, practical farm observations have been reported from practically all of them.

Cobalt: Probably the observations on cobalt deficiency have been most widespread in this area. Cobalt deficiency, or response to cobalt supplements with animals under natural conditions in farm practice, has been observed in New Hampshire, Vermont, New York, North Carolina, Ohio, South Carolina, Virginia, Georgia, and possibly Maine. Conditions which could be associated with cobalt deficiency have been noted in other states, notably Louisiana, Mississippi, Maine and Kentucky, but even the dubious confirmation of response to cobalt in a mineral mixture has not been reported.

The close resemblance of cobalt deficiency symptoms and starvation for lack of total digestible nutrients makes identification difficult. Further, Beeson and associates at Ithaca, New York, have observed that alfalfa has always been found to contain an adequate nutritional level of cobalt. Thus, if alfalfa were given to poor cattle suffering from either cobalt deficiency or lack of total digestible nutrients, favorable response should re-

sult.

Two factors have led to the widespread use of cobalt supplements in mineral mixtures and feeds in the recognized deficiency

areas and in many suspected areas of the East and South.

First has been the development of symptoms, including loss of appetite, weight loss, drop in milk production, anemia, failure to shed the old hair in the Spring, and indifferent reproductive performance, even when the total digestible nutrients were available in quantity if not quality.

Second has been the rapid improvement of such animals when

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fed cobalt supplements. This response has been observed where chemical analyses have failed to detect differences in the cobalt content of feed or animals. The low level of cobalt requirement in ruminants, 0.1 part per million in the feed, has made detection of deficiency situations quite difficult.

Cobalt deficiency has been well studied in North Carolina in cooperative work between the Regional Laboratory in Ithaca, New York, and the North Carolina Experiment Station at Raleigh, particularly in the coastal areas. Detailed studies have been carried out on plants, animals and soils. Cobalt is deficient here and response is obtained in cattle on those areas. In fact, cattle can be kept on those areas now which previously could not be expected to survive due to the low cobalt intake. The soil types in the coastal plain of South Carolina and Georgia closely resemble the deficient soils in Florida, and in these areas cobalt has given a response, although little experimental work has been carried out. It has been the experience of farmers and research men in commercial enterprises that the addition of cobalt gives a favorable response over large areas of these states.

Copper: Copper, which is also needed by cattle in many of these same areas, has given definite response to beef cattle and dairy cattle in the eastern part of Virginia. Presumably this deficiency has resulted from repeated cropping and possibly from practices which have caused a fixation of the copper. It has been reported as a deficiency in Kentucky, Louisiana and Mississippi.

In Kentucky areas, the copper deficiency is not complicated by the presence of molybdenum, but chemical analysis has shown forage copper levels as low or lower than one part per million. Similar observations have been made in Louisiana. The animals exhibit imperfect performance, breeding troubles and anemia, with response to the addition of copper as copper salts either as mineral supplements or through the addition of copper as fertilizer. This has been particularly true in Kentucky where young horses and cattle on these areas have shown some of the changes noted in cattle in the Everglades area of Florida. Response has been rapid, when a supplement of copper has been introduced. Critical evaluation has yet to be made, but the improvement in foal development has convinced thoroughbred owners that copper is necessary as a trace element. Deficiencies have not developed that are associated with interfering elements such as molybdenum, which in some areas causes deficiency symptoms to develop. In some of the alluvial soils of Louisiana and Mississippi, there have been observed changes suggestive of copper deficiency. Graying of the haircoat has been noticed in Louisiana and this has been attributed to a lack of copper or to abnormal copper relationships with other minor elements.

Molybdenum: Molybdenum toxicity problems have not been observed in the states indicated except in some parts of New

Jersey. In some alfalfa, abnormally high levels of molybdenum have been observed and associated with animal changes. In these areas, copper was at a low level, and symptoms similar to changes observed in the copper deficient soils of Florida were noted. That these conditions are not extensive may reflect the fact that the grazing season is short and, therefore, the animals have not developed the abnormal conditions before they are given supplements which correct largely some of the unbalanced mineral intakes.

Iron: Iron should be mentioned as a trace element that is

involved in the nutrition of livestock.

In some parts of South Carolina, there are out-croppings in the coastal plain of iron-bearing rock and these have been known for many years as wild animal licks. Domestic cattle grazed in these same areas will use these out-croppings as licks, consuming the rock in appreciable amounts. The sodium chloride level is very low in these rocks. Iron is the principal trace element pres-

ent, with a very small amount of copper.

It has been suggested that this is a sign of nutritional deficiency. The wild animals have been observed to use these only in the late summer or fall and the suggestion has been made that due to blood loss from insect attack during the summer, the demand for these minor elements is such as to lead them to make use of these out-croppings. This is an interesting speculation and perhaps some day a logical explanation will be obtained. At the present time, it can only be mentioned that this observation has been made and suggest that perhaps the animals do have a desire or a liking for the particular rock that appears in the otherwise sandy soils of this area.

In summary, it may be mentioned that cobalt deficiency has been observed in many of the states of the East and South of the U.S.A. and cobalt supplements in feed are common. Copper deficiency has been observed in at least five of the Southern states, including Florida. The deficiency has been less severe than has been observed in some parts of Florida, perhaps attributable to the lack of complicating factors such as the presence of molybdenum. Molybdenum has been found in some areas at levels higher than nutritionally desirable, but may be associated with continued fertilizer applications that have resulted in building up the molybdenum content of these soils to a point where legumes may contain amounts sufficient to interfere with animal nutrition if the copper intake is low.

# WORK ON TRACE ELEMENTS IN ENGLAND, SCOTLAND AND IRELAND\*

### KATHERINE WARINGTON\*\*

The earliest experiments on trace elements in Great Britain arose out of a bequest made in 1896 by Mr. E. H. Hills to the Royal Agricultural Society of England, for the purpose of determining the value of what he termed "the rarer forms of ash." Under this heading he included constituents such as fluorine. manganese, iodine, bromine, titanium and lithium. As a result, a series of pot culture experiments in soil was carried out by Voelcker at the Woburn Experimental Station, from 1897-1920, to test the possible benefit of these and other elements on wheat and barley (41). In some instances, provided only small quantities of the substance were used, a stimulating effect on the plant was obtained, but large doses invariably proved harmful. In 1910, at much the same time as French workers were obtaining beneficial results from the use of boron, manganese, and zinc compounds, (1, 2, 4, 5, 27) Brenchley began a series of investigations at Rothamsted on the action of arsenic, boron, copper, manganese and zinc on plants grown in nutrient solutions (8, 9). Though no evidence was forthcoming from her preliminary experiments that any of these elements were essential for growth, nevertheless a much better understanding of their mode of action was thereby obtained and interest in the possibilities of their practical application aroused. After a break of about ten years, work was resumed on the question, special attention being paid to the action of boron, and in 1923 Warington (46) obtained conclusive evidence that this element was essential for the normal development of at least certain of the higher plants. A series of investigations followed, each dealing with different aspects of the subject, with a view to determining the part played by boron in plant metabolism. This hope, however, was not realized, and in fact the question remains largely unsolved even today. At the same time, a good deal of light was thrown on the effects of a deficiency of the element on the plant. Perhaps the most important result was the discovery by Brenchley and Thornton (11) that boron was required for the proper development and functioning of the nodule in leguminous plants. In the absence of boron, the vascular supply to the nodule was found to be defective, while the bacteriod tissue, and in consequence the quantity of nitrogen fixed, was markedly reduced. From anatomical studies by Warington (47) and later by Rowe (38), it was clear that meristems were particularly dependent on a continual supply of boron, hypertrophy and break down of these tissues oc-

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<sup>\*-</sup>Presented by Dr. Roy A. Bain, Agronomist, Everglades Experiment Station, Belle Glade.

curring in its absence. In the event of a renewal of the supply of boron, however, new and healthy meristems could develop (50), and Brenchley and Watson (14) obtained normal flowering in sugar beet plants which had suffered from severe heart rot in their first year of growth, following an application of boron in the second year, a finding of some practical importance to the seeds merchant. Among other results of these investigations, mention may be made of the indications of an association between boron and calcium nutrition obtained by Brenchley and Warington, (12, 48) which has since been confirmed and developed by various workers in other countries.

Boron deficiency diseases in the field, though frequently recorded in Great Britain for crops such as turnip, swede and sugar beet, have never attained a position of large-scale economic importance as they have in other parts of the world. Consequently the work on the practical side has not been very extensive.

Manganese deficiency, however, is of considerable importance in certain parts of England and much of the work with this element has been concerned with the practical aspects of the problem. In 1940, Wallace, of the Long Ashton Research Station, carried out a survey of soil types in England on which manganese deficiency had been reported for horticultural or agricultural crops (42). The trouble was found to be chiefly associated with the peaty soils of the Fen district, Romney Marsh in Kent and with areas in the West Midlands and Somerset, though it was liable to appear on newly ploughed up grassland and on reclaimed heaths. As has been found in other countries, the soils concerned were not necessarily low in total manganese, but invariably had a high organic matter content and a pH of 6.5 or more. Questions of availability were clearly involved, and from the work of Heintze and Mann at Rothamsted (22), it seems that under these conditions the manganese may become locked up in a non-available form as complexes with the organic matter in the soil. Other investigations by Dion in conjunction with these workers, have been concerned with the fractionation of various forms of manganese and manganese higher oxides in different types of soil (15). Crops vary widely in their demand for manganese. In cereals it is particularly high, though even in this group considerable varietal differences are exhibited, as Gallagher and Walsh (17) working in Ireland have found. Leguminous crops such as clover, on the other hand, generally have a low manganese requirement, but peas are very sensitive to any shortage, Heintze (20) in 1938 showing that marsh spot disease was due to a lack of manganese in the soil. The important part played by nitrogen in determining the incidence of marsh spot was evident from her later work (21), where she induced symptoms of the disease in peas grown on soils rich in available manganese, by injecting simple inorganic and organic nitrogen compounds into the plant. Healthy peas were found by Glasscock and Wain (18) at Wve College to contain more manganese than those affected with marsh spot, but according to later work by Walsh and Cullinan (45), both healthy and diseased seeds in the same pod may have a very similar manganese content. With regard to remedial measures, spraying the plant with a solution containing manganese has been recommended both by Lewis (30) and Wallace and Ogilvie (44) in preference to soil applications. Correct timing of the treatment is important, and peas should not be sprayed before the flowering stage, if marsh spot is to be avoided.

Damage from excess manganese is uncommon in Great Britain, but the question has not been overlooked and both Wallace, Hewitt and Nicholas at Long Ashton (43), and Hale and Heintze (19) at Rothamsted have produced evidence of manganese toxicity in crops grown on acid soils.

Work on the function of manganese has been taken up comparatively recently in England. In 1948, Hewitt (24) made a study of the relationship between manganese and iron nutrition, showing that symptoms of iron deficiency induced by excess manganese or other heavy metals were not identical with those caused by a simple lack of iron. From this he concluded that the two elements have at least some independent functions in the plant metabolism. In conjunction with Jones and Williams (26), he was able to confirm the accumulation of nitrate in manganese and molybdenum deficient plants, and from a study of the aminoacid concentration in each case, to suggest that though the two elements are both required in the process of nitrate reduction, they probably function in different parts of the chain of reactions.

Some of the latest work with manganese has been on the biochemical side. Peroxidase preparations from horse-radish and turnip have been shown by Kenten and Mann (28, 29) at Rothamsted to oxidize manganous salts in the presence of certain phenolic substances and hydrogen peroxide. From their results, they put forward the hypothesis that the manganese reduced the oxidized peroxidase substrate, thereby becoming involved in an oxidation-reduction cycle, a theory which would be in keeping with the view that manganese plays a part in the

processes of respiration.

Investigations on the effect of molybdenum on higher plants have been comparatively recent in Great Britain as elsewhere, though in 1934 Sheffield (39) had demonstrated cytological abnormalities in solanaceous plants treated with molybdates, while Warington (49) found that tannin-molybdenum compounds accounted for the yellow colouration in tubers of potatoes grown with excess molybdenum. Indications that the element was essential for lettuce were obtained in 1942-46 (13, 51) during the course of investigations at Rothamsted regarding the trace element constituents of Chilean nitrate, shortly after workers in other countries had proved that molybdenum was needed by tomato and oats (3, 34). More recently, Hewitt and Jones (25)

have made a special study of molybdenum deficiency effects on tomato and brassica crops, confirming the association of "whiptail" disease of cauliflower with a lack of this element (Figures 1 & 2).

Results regarding the harmful action of excess molybdenum on plants have proved somewhat conflicting, and in a series of



Figure 1.—Whiptail in Cauliflower grown in sand culture without molybdenum. E. J. Hewitt and E. W. Jones. Long Ashton Research Station.



Figure 2.—Molybdenum deficiency in Savoy Cabbage. L. Control. R. Without Mo. E. J. Hewitt and E. W. Jones. Long Ashton Research Station.

pot cultures in 1948, Brenchley (10) was able to show that the degree of toxicity depended both on the type of soil and the species of plant grown. For example, the harmful action of a specific dose of sodium molybdate was greater on a sandy soil compared with a black fen or clay soil (figures 3 & 4), but on the same soil, tomato might be uninjured by a dressing which



Figure 3.—Solanum nodiflorum in sandy soil. L-R. No Mo, Low Mo, High Mo. W. E. Brenchley. Rothamsted Experimental Station.



Figure 4.—Solanum nodiflorum in clay soil. L-R, No Mo, Low Mo, High Mo. W. E. Brenchley. Rothamsted Experimental Station.

was very poisonous to flax and fatal to *Solanum nodiflorum*. The fact that different plants may vary in molybdenum content when grown on the same soil has a practical bearing on the occurrence of "teart" in cattle, a disease due to molybdenum poisoning. Ferguson, Lewis, and Watson (16) at Jealott's Hill Research Station found, for example, that the risk was greatest when the proportion of clovers in the pasture was high, since legumes absorbed molybdenum more readily than grasses, and further, that the molybdenum content of herbage varied considerably with its stage of growth:

Instances of deficiencies of other trace elements have so far been isolated only, though benefit from zinc treatment has been reported for cherries by Thompson and Roberts (40) in 1945, and for cereals and potatoes by Roach and Barclay (37) in the following year. More recently Bould and others (6) described a failure of fruit trees due to a lack of zinc and have since found apples suffering from copper deficiency in the same district (7). A favourable effect from copper sprays has also been reported by Muskett (33) from Ireland. Such deficiency troubles, however, seem unlikely to become a large scale problem in Great Britain, though they will probably continue to arise in certain localized areas.

The correct diagnosis of symptoms of mineral deficiency or toxicity in a plant is naturally an essential before remedial measures can be applied. A valuable contribution to a better understanding of this aspect of the subject in the case of trace elements has been made at Long Ashton by Hewitt (23), who has developed a pot culture technique, using containers coated with bituminous paint and specially purified water, salts and sand. Under these controlled conditions, deficiency symptoms, of which the cause is known, can be produced in plants for comparison with field grown crops. Another method of approach has been adopted at East Malling Research Station. Here leaf analyses and response to leaf injection have been used by Roach (35) and others to diagnose any deficiency in the mineral status of the plant, and improved yields, based on the findings, obtained even when the crop failed to exhibit any visual symptoms of the trouble. The whole subject of injection has been studied in great detail by these workers, during the past ten years or so, one outcome of which has been the development of a technique suitable as a curative measure for fruit trees. Some of the most recent experiments by Roach (36) in 1947, however, emphasize the need for testing treatments based on any method of diagnosis with the subsequent performance of the crop, as in some cases the expected correlation was lacking.

All trace element studies call for specially refined analytical methods, both for purpose of rapid survey and exact quantitative measurement. Mitchell (31, 32), at the Macaulay Institute in Scotland, has worked out spectrographic techniques suitable for the geochemical study of rocks and the determination of trace

constituents in soil extracts and plant material, and it is now possible to estimate up to fifteen of these elements simultaneously.

The course of the investigations on the trace elements essential to higher plants seems to have followed a logical sequence, the first phases of which have been brought to a successful conclusion. Proof of the necessity of the elements has been obtained, the effect of their deficiency on various crops studied in some detail, and appropriate remedial measures developed. The most difficult stage has now been reached, namely that of determining the function or functions of the elements in plant metabolism. Mention has already been made of the probable part played by both manganese and molybdenum in nitrate reduction and the association of boron with calcium nutrition. It seems likely, however, that with the possible exception of boron, most of the essential trace elements will prove to be mainly concerned with enzymatic processes. Copper containing enzymes are already known, while zinc is thought to play a part in the activity of plant carbonic anhydrase. Future work may well show that manganese functions in some analagous manner. Many questions regarding availability of the elements to the plant remain unanswered, and in this field the help of the soil chemist will be needed. Fresh inter-relationships between the various elements are constantly being discovered, though their nature is not yet understood. The presence of cobalt in the soil, for example, apparently increases the uptake of molybdenum by the crop, while the addition of copper may produce symptoms of manganese deficiency in the plant. In addition, little is known of the part played by micro-organisms and developments in this field may be expected. The importance of the trace elements in plant life is now firmly established, but the co-operation of workers in many branches of research will be needed before their function is fully understood.

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# INVESTIGATIONS ON TRACE ELEMENTS IN THE NETHERLANDS\*

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Introduction.

The beneficial effect of trace elements on plant growth in the Netherlands was shown for the first time by Sjollema and Hudig in experiments on a disease of oats on neutral and slightly alkaline peaty soils (14). Although in those days Hudig was of the opinion that this effect of manganese had to be attributed to the correction of some unfavourable condition of the organic matter, it was shown by further investigations that the oats disease was caused by lack of available manganese. Söhngen (16) and particularly Gerretsen (6) demonstrated the effect of microorganisms in rendering soluble manganese compounds in soil unavailable for the plants.

In 1924 it was found by Hudig and Meyer (7) that the socalled reclamation disease which was found on newly reclaimed peaty and sandy soils in the Netherlands may be cured by adding copper sulphate to the soil. In the same way as with manganese, the beneficial influence of the heavy metal was attributed to some mysterious effect on the soil organic matter. Other investigators were of the opinion that the disease was caused by microorganisms (2). Copper should have a disinfecting effect. After the discovery of the indispensability of copper for plant growth (Sommer (15), Brandenburg (3)), it was shown by the author (10) that the reclamation disease is caused by copper deficiency of the plants.

In 1933 Sjollema published a report on copper deficiency in cattle (licking disease) which was found in areas where the

plants suffered from the reclamation disease (13).

In addition to manganese and copper a beneficial effect of iron, zinc, boron and molybdenum on plant growth has been found in the Netherlands.\*\*\* More details concerning these elements will be given below.

Occurrence of trace element deficiencies in the Netherlands.

Iron deficiency is found only sporadically in agricultural crops in the Netherlands. In horticulture this element is of more importance.

Manganese deficiency may be found on sandy and peaty soils

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\*\*\*—Magnesium is not listed to the trace elements by the author. Therefore

the investigations carried out on this element will not be recorded in this lecture.

where the reaction is approximately neutral. After the extensive investigations carried out by Dutch workers in the past, this fact is well-known by the farmers and therefore the reaction on this type of soil is maintained mostly between pH 5.0 and 5.6. At these values no manganese deficiency of the plants will be found.

On some clay soils containing a certain amount of organic matter and with a high content of calcium carbonate, where manganese deficiency also may be found, this adjustment of pH is not feasible. This is particularly the case on the light clay and sandy soils in the young polders of the Zuiderzee, which may contain more than 10 percent of calcium carbonate. Here applications of manganese salts have to be carried out every year. In some cases spraying of the crops with a 1.0-1.5 percent solution of manganese sulphate appeared to be more successful than application of the salt on the soil.

According to Gerretsen of this Experiment Station the insolubilization of manganese in neutral soils containing a certain amount of organic matter has to be attributed to the activity of

microorganisms (6).

In liming experiments on a lowmoor peat containing a high amount of clay, carried out by the author, no manganese deficiency was observed within a period of 10 years after liming of the soil. It is unknown whether this result was due to the absence of manganese-oxidizing microorganisms or to the particular condition of the soil organic matter.

Zinc deficiency is found on apple, pear and cherry trees growing on soil very rich in phosphate (9).\*

Copper deficiency (reclamation disease) may be found on sandy and peat soils, particularly shortly after reclamation of these soils. It is well-known by the farmers that under these circumstances they have to apply 50-100 kg of copper sulphate per ha. Therefore heavy symptoms of copper deficiency are found only sporadically in agricultural crops. A slight increase in yield after a copper dressing may be obtained rather frequently. More recently copper deficiency has been observed in orchards by Dr. D. Mulder, Laboratorium van Zeelands Proeftuin, Goes.

As to the occurrence of copper deficiency in animals the situation is more complicated. On soils poor in available copper, cattle may show symptoms of copper deficiency (licking disease). In some cases, however, a beneficial effect of feeding small amounts of copper to cattle has been observed notwithstanding the herbage which was fed had a normal copper content. This result is obtained particularly in the reclaimed North West polder of the Zuiderzee. Apparently uptake of copper from the food may be affected by some unknown factor. Although it is sometimes supposed that excess of molybdenum in the herbage may

<sup>\*—</sup>Dr Gerretsen at this Station has worked out a micro-biological method to estimate available zinc in soil.

be the cause of the high copper requirement, more evidence is needed to confirm this hypothesis.

Boron deficiency may be found rather sporadically on sandy soils in the South of the country and on river-clay soils. Besides beets and turnips, leguminous crops may respond sometimes to small amounts of this element. In experiments with peas the author has shown that on boron deficient soils nitrogen fixation may be badly affected as a result of which the plants become deficient in nitrogen and die at an early date (11).

Recent investigations on trace elements carried out in the Netherlands.

During the last 15 years much work has been done by the author on the effect of copper and molybdenum on plant growth and on some physiological phenomena in both higher plants and microorganisms. These investigations started in 1935 when an extensive study was undertaken to elucidate the role of copper in preventing the socalled reclamation disease in plants. This disease which may occur on sandy and peaty soils particularly when they are newly reclaimed, occurs in many areas of Western Europe as well as in the U.S.A. and Australia.

To prove that the reclamation disease has to be attributed to a lack of plant-available copper the following three sets of ex-

periments were undertaken.

a) A comparison was made of the symptoms of copper deficiency in culture solutions with those of the reclamation disease.

These symptoms appeared to be quite similar. This was not only true of the pronounced cases in which dead white tips occur at the youngest leaves of cereals and no ears emerge, but also of the light cases in which the ears emerge normally but the grain production is reduced. Plant species less susceptible to the reclamation disease (potatoes, rye) required less copper than highly susceptible plants like wheat, barley and oats. In addition the former have a greater absorption capacity for less available soil copper than the latter. This was concluded from the fact that the difference in copper requirement between both groups of plants growing in soil is much greater than when growing in nutrient solutions.

A crop very susceptible to copper deficiency is canary grass (*Phalaris canariensis*) which was successfully used by the author

in pot tests as an indicator plant for copper deficiency.

When a comparison is made of the amounts of copper required for normal plant growth in nutrient solution and in peaty or sandy soil, it will be found that in the former case an amount of  $50 \ r^*$  of copper per  $2 \ l$  of nutrient solution, added only once, is enough to secure normal plant growth. When ap-

<sup>\*</sup> $_r = gamma$ , here and elsewhere below.

plied to the soil 5 mg. of copper per 2 kg of soil are required. This discrepancy is caused by the fixation of copper by soil organic matter. This was demonstrated by employing the root separation technique. One half of a cylinder was filled with "diseased" soil, the other half, separated by a glass plate, with quartz sand or with a nutrient solution. Plants were grown with part of their roots in the soil and the other part in the sand or the nutrient medium. When the copper was added to the nutrient-solution half, amounts similar to those required in the culture solution experiments were able to give normal plants. When added to the soil half, twenty times greater amounts of copper were unable to give normal plants.

- b) Copper determinations were carried out in plants grown on normal and "diseased soils." In the latter case much lower copper values were obtained than in cereals grown on "healthy" soils.
- c) Plant available copper was determined in the soil by using a microbiological assay. This method is based on the fact that the fungus Aspergillus niger requires small amounts of copper for the development of normal black spores. In a nutrient solution purified from copper this fungus develops a white sterile mycelium. With 0.2r of copper in 40 cc of nutrient solution yellow spores are formed, with 0.4r the colour of the spores is yellowish brown, with 1.0r grey-brown, with 1.5r grey-black, while 2.5r of available copper and higher amounts give black spores. For the estimation of available copper in soil one gram of airdied soil is added to 40 cc of a purified nutrient solution in 1 l Erlenmeyer flasks. This medium is inoculated with a suspension of Aspergillus spores and after 4 days of incubation at  $30^{\circ}$  C the colour of the mycelia is compared with the colour scale of a set of standard cultures to which different amounts of copper have been added.

A great number of "diseased" and normal soils from different parts of the Netherlands were tested for available copper according to the above method. Part of the results is given in Table 1.

From these figures it will be seen that soils on which the plants show symptoms of the reclamation disease have a very low content of available copper. Soils on which the plant growth is normal have a considerable higher copper content.

The results of these experiments clearly show that the reclamation disease is brought about by a lack of available copper in the soil.

<sup>†—</sup>The microbiological assay is employed by the Soil Testing Laboratory at Groningen to test soil samples for available copper. The method is modified by Dr. Gerretsen of this Experiment Station in order to be able to estimate amounts of available copper in the range—15r per gram of soil. This is possible by doubling the concentration of nutrients in the solution.

TABLE 1 .- PLANT GROWTH AND AVAILABLE-COPPER CONTENT

Soil	Plant growth	Aspergillus-available copper per 1 g of air-dried soil, r		
Sandy soil	Normal wheat	> 2.5		
Sandy soil	Normal white oats	> 2.5		
Sandy soil	White oats, severely diseased	0.1		
Sandy soil	White oats, moderately diseased	1.1		
Sandy soil	White oats, normal	1.5		
Sandy soil	White oats, normal	2.5		
Sandy soil	White oats, diseased	0.3		
Peaty soil	Wheat, severely diseased, rye normal			
Sandy soil	Normal wheat	> 2.5		
Sandy soil	Normal canary grass	$> \overline{2.5}$		
Peaty soil	Normal wheat	$> \overline{2.5}$		
Peaty soil	Normal wheat	$\lesssim 2.5$		
Sandy soil	Normal wheat	2.5		
Sandy soil	Wheat, slightly diseased	1		
	White oats, normal	1.8		
Sandy soil	White oats, diseased	0.4		
Sandy soil	White oats, severely diseased	0.2		
Sandy soil		0.1		
Peaty soil	White oats, severely diseased Wheat, slightly diseased	1		
Peaty soil		0.25		
Sandy soil	White oats, severely diseased	0.23		
Same field	Slightly diseased area			
Same field	Normal area	1.70		
Same field	Plants cured by copper sulfate	> 2.50		
Peaty soil	Wheat, severely diseased	0.20		
Same field	Normal area	22.5		

<sup>\*-</sup>r = gamma

The low content of available copper is often a result of the presence in the soil of black humus. This was shown in experiments with  $Aspergillus\ niger$  and also in percolation experiments. In the former copper sulfate was added in different amounts to the black humus from a healthy soil very poor in available copper. The mixture was incubated for 24 hours at room temperature, sterilized at  $110^{\circ}$  C for 10 minutes and thereafter added to a copper-free nutrient solution of  $Aspergillus\ niger$ . The following results were obtained.

	Fungus available copper
2  g black heath humus (total copper  2.6r)	0.2r
2  g black heath humus $+ 3r$ Cu, as sulphate, adde	d = 0.6r
2  g black heath humus + 5r  Cu, as sulphate, adde	d = 0.8r
2 g black heath humus + 10r Cu, as sulphate add	led 10r
2  g black heath humus + 20r  Cu, as sulphate, add	$1  ext{led} 2.0r$

It will be seen that this black humus fixed added copper to a considerable degree.

In a subsequent experiment a sandy soil very poor in plant-available copper was percolated with a 0.25 percent copper sulphate solution for 8-10 hours with a speed of 100 cc per hour. Then the soil was washed with distilled water until a practically

negative reaction on copper by carbamate reagent was obtained. Subsequently the soil was percolated with a solution of 1 percent calcium nitrate until no more than 2r of copper per 10 cc of liquid was washed out. Then the exchanged and still bound copper were determined. The following figures were obtained:

Soil with severe	Exchanged by $Ca(NO_3)_2$ (per 1 g. of org. matter).	Retained in soil (per 1 g. of org. matter).	
copper deficiency	46.7 mg Cu	24.3 mg Cu	
Normal soil	37.8 mg Cu	5.1 mg Cu	

These data show that in the copper-deficient soil the total amount of copper which can be retained after treatment with distilled water is considerably higher than in the normal soil. Of this copper 34 percent was not liberated after treatment with calcium nitrate. In the normal soil only 11.5 percent was retained after treatment with calcium nitrate.

In a subsequent experiment the same copper-deficient soil was compared with a peaty soil on which plants grew normally. In this case the total amount of copper which was retained by the copper-deficient soil after removal of the excess copper sulphate with distilled water was also nearly twice as high as the amount retained by the normal soil. Upon treatment with ½ N hydrochloric acid practically all of the copper was liberated from both soils.

Fixation of copper by hydrogen-sulphide producing bacteria.

In experiments with *Aspergillus niger* and cereals it was found that copper precipitated by hydrogen-sulphide forming bacteria was unavailable. Since copper precipitated chemically by hydrogen sulphide is readily absorbed by *Aspergillus* as well as by higher plants it must be assumed that the copper compound formed by the microorganisms is either copper sulphide, present inside the bacteria cell, so that it is protected from being oxidized, or is not copper sulphide.

In experiments with sterile cultures of barley and oats similar symptoms of copper deficiency were obtained as in solutions

which were not sterilized.

Interaction of copper and other nutrients.

Copper-Manganese. Application of copper sulphate to copper-deficient soils sometimes may result in the appearance of manganese deficiency in the plants grown on these soils (8). Although the possibility that such soils are deficient in available manganese as well as in available copper may not be excluded, evidence is available that copper may catalyze the oxidation of

available manganese to less soluble compounds. Although it is unknown to what extent the insolubilization of manganese in soil has to be attributed to microbial activity, it is rather simple to demonstrate the oxidation of manganese compounds to manganic oxide by microorganisms (Gerretsen (6), Sohngen (16), Beyerinck (1). The author isolated a manganese-oxidizing fungus and studied the effect of copper on its capacity to oxidize manganous to manganic compounds. It appeared that traces of copper stimulated the formation of black manganic oxides to a considerable extent (10). Although it is unknown whether in copper-deficient soil a similar stimulation may occur after application of a copper salt, it is likely that under certain circumstances this may be true.

In an experiment with rye in nutrient solutions a clear effect of copper on manganese deficiency of the plants was observed. In this experiment copper was added in amounts of 0, 2, 10 and 50 r per culture. When the plants were about one month old, heavy symptoms of manganese deficiency were observed in the solutions supplied with 50 r of Cu. Those with 10 r were free from manganese deficiency. Some vessels were supplied with 3 mg of  $MnSO_4$ ; they recovered within a few days (Table 2). It is unknown whether in this experiment copper has stimulated the oxidation of manganese in the nutrient solution (the nutrient medium was not sterile) or that precipitation has taken

place in the plant tissue.

TABLE 2.—Effect of Copper Supply on Manganese Deficiency in Rye.

Copper, r/pot	0.2 mg MnS	O <sub>+</sub> . 4 H <sub>2</sub> O	3 mg MnSO <sub>4</sub> . 4 H <sub>2</sub> O	
	Grain, g	Straw, g	Grain, g	Straw, g
0 2 10 50	0 0 0.2 0	1.17 3.18 9.06 1.18	0 0 1.04 0.15	0.61 5.08 6.43 5.03

In barley, oats and wheat no effect of copper on the manganese supply was observed.

Copper-Zinc, Copper-Iron.

In culture solution experiments with different amounts of copper, zinc and iron no interaction between copper and zinc and copper and iron was observed (barley).

Copper-Cadmium.

In experiments with *Aspergillis niger* a clear interaction of cadmium and copper was observed. With increased amounts of cadmium more copper had to be supplied to induce black spores (Table 3). In barley no effect was observed.

TABLE 3.—Effect of Cadmium Sulphate on Colour of Aspergillus Spores Supplied With Different Amounts of Copper.

3 Cd SO <sub>4</sub> . 8 H <sub>2</sub> O	No copper supplied	2r Cu	6r Cu	20r Cu
0 25 50 100 200 500 1000 2000	bright yellow bright yellow bright yellow bright yellow no spores no spores no spores	black black brown-black brown-black gray-brown yellow yellow yellow	black black black black brown-black brown-black brown yellow-brown	black black black black black brown-black brown-black brown

# Copper-Nitrogen.

In pot experiments with wheat growing in a copper-deficient soil supplied with different amounts of copper and nitrogen (as ammonium nitrate), an interaction between copper and nitrogen was observed. In the absence of supplied nitrogen and copper, small but entirely normal plants developed which were able to produce normal seeds. Supplied with a small amount of nitrogen, heavy symptoms of copper deficiency appeared and no grains were produced. As will be seen from Fig. 1, increasing amounts of added ammonium nitrate required increasing amounts of copper to obtain normal plants.

# Physiological effect of copper.

Copper plays a role as the prosthetic group of oxidizing enzymes (tyrosinase, laccase, ascorbinase etc.). Apparently due to this function the effect of copper on a number of oxydation reactions, studied by the author, may be explained. These reactions are: a) blackening of Aspergillus niger spores, b) blackening of aging cultures of Azotobacter chroococcum, c) oxidation of manganous compounds to manganic oxid by fungi, d) transformation of aethyl alcohol to acetic acid by Acetobacter aceti (10).

More recently the effect of copper on tyrosinase activity in potato tubers was investigated in the author's laboratory. In an extensive study on the blackening of potassium-deficient potato tubers it was found that this phenomenon is due to the oxidation of tyrosine to red and then black oxidation products by tyrosinase. This reaction can proceed only when the cells are injured, so that tyrosine is subjected to tyrosinase activity. Potassium-deficient tubers are much more liable to injury than those with a normal potassium supply. In addition their tyrosine content is much higher (12). Both factors are responsible for the blackening.

When potatoes are cultivated on soils poor in available copper and poor in available potassium, blackening of bruised tubers

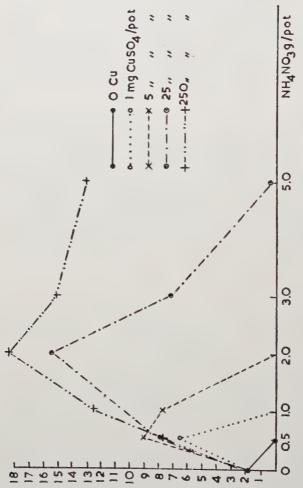


Figure 1.—Interaction of copper and nitrogen (Pot experiment with wheat) Yield on ordinate is grams grain per pot.

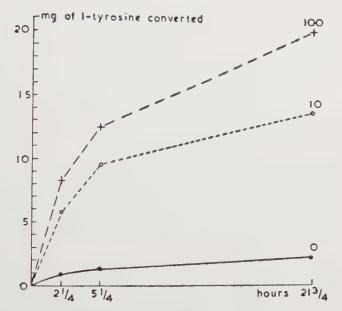


Figure 2.—Effect of the supply of copper to potatoes on the tyrosinase activity in the tubers. On the Chart:

0 no copper supplied
10 copper sulfate, 10 kg./ha.
100 copper sulfate, 100 kg./ha.

occurs only to a small extent. This is due to the low tyrosinase activity of potatoes poor in copper (Fig. 2).

The question may be put whether or not tyrosinase plays the part of a terminal oxidase in the respiration of potato tubers. Although some authors are of the opinion that this is true, little evidence can be found in literature.

In the author's experiments no difference in respiration rate of copper-deficient and normal tubers was observed. Infiltration of tuber slices with the copper reagent diaethyl-dithio-carbamate gave a considerable decrease of carbon dioxide output, however, indicating that copper may be of considerable interest in respiration. These investigations are being continued.

Effect of molybdenum on plant growth and nitrogen metabolism of plants and microorganisms.

A second trace element which has been studied extensively by the author in the last few years is molybdenum. In comparison with copper it is required by higher plants and microorganisms in considerably lower amounts.

Some years ago the effect of molybdenum on growth and nitrogen metabolism of a number of higher plants and micro-

organisms was studied. From these investigations which are published in Plant and Soil 1, 94, 1948, the following conclusions may be drawn:

a) Molybdenum is an essential element for the normal development of green plants and a number of microorganisms.

b) In the green plant as well as in the cells of bacteria and fungi, molybdenum is required for the *assimilation of nitrate* nitrogen. This was shown in experiments with tomato and barley plants and with denitrifying bacteria and the fungus *Aspergillus niger*.

c) Molybdenum is essential for the fixation of nitrogen by free-living bacteria as well as by symbiotic bacteria (Rhizobium). In experiments with peas many nodules developed on the roots in nutrient solution without supplied molybdenum but the nitrogen fixation of these nodules was insignificant so that the plants became nitrogen-deficient and died at an early stage.

### Experiments with soil.

In order to investigate whether or not molybdenum deficiency might occur in Dutch soils, pot and field experiments were carried with peas on soils where the pea growth was poor. No effect of molybdenum application was observed so that it was concluded that molybdenum deficiency did not occur in the Netherlands.

After the war some pot experiments were carried out with molybdenum-deficient soil received from Australia by courtesy of Professor Prescott, Waite Institute, Adelaide. A clear response to molybdenum was found in white clover and subterranean clover but not in pea (Table 4). Since the Australian soils used in these experiments were rich in ironstone and rather acid, pot experiments were undertaken with an acid lowmoor peat soil, rich in ironstone, from the province of Groningen (organic matter 60 percent, pH 5.0).

TABLE 4.—Effect of Molybdenum on Yield and Nitrogen Fixation of Clover, Grown in Australian Soils.

Soil received from	Нq	$Na_2MoO_4$ . 2 $H_2O$ per pot (2 kg soil) mg.	White Yield, g Dry-wt.	Nitrogen	Subterran Yield, g Dry-wt.	ean clover Nitrogen mg.
Tasmania	6.2	0	4.2	110.5	. 12.9	272.0
Tasmania	6.2	5	12.2	382.0	16.8	428.5
S. Australia	5.4	0	4.3	93.4	11.1	243.0
S. Australia	5.4	5	5.9	170.0	17.3	395.0

In agreement with the results obtained with the Australian soils a big response to molybdenum was observed in white and red clover. Without application of molybdenum many nodules had developed in both plant species. These nodules were smaller than those of plants supplied with molybdenum, whereas the colour was not pinkish as usual but yellow or brown-gray. Nitrogen fixation was quite inadequate, as a result of which the plants became pale green and grew much poorer than those supplied with traces of molybdenum. With improved molybdenum supply the number of nodules decreased but their nitrogen fixing capacity increased considerably (Table 5).

TABLE 5.—Effect of Applications of Molybdenum on Nitrogen Fixation and Yield of White Clover Grown on an Acid Lowmoor Peat Soil Rich in Ironstone.

Na-MoO., 2 H <sub>2</sub> O applied per pot†	Dry weight g. per pot*	Nitrogen in plants, per pot, mg.*	Number of nodules per 173 cm² bottom of glass cylinder*	Molybdenum in plants mg. per kg of dry matter*
$\begin{array}{c} 0\\10\\50\end{array}$	2.1	51.6	$\begin{array}{c} 456 \\ 368 \end{array}$	< 1
10 50	2.7	71.7 $131.0$	$\begin{array}{c} 368 \\ 254 \end{array}$	1.8
100	4.1 4.7	152.0	151	2.4 3.7 4.3
500	4.8	158.7	151 87	4.3
1000	4.8	155.0	$\frac{116}{123}$	3.3 6.5
2500	4.7	150.0	123	6.5
5000	4.6	147.9	116	13.7
10000	4.8	151.0	107	25.4
20000	3.8	127.0	109	80.0
50000	4.4	147.0	70	183.1

<sup>†-</sup>Each pot contained about 500 g of soil.

\*-Averages of duplicate values

As will be seen from these results, optimal nitrogen fixation of white clover was attained already at 100~r Na<sub>2</sub>MoO<sub>4</sub>. 2 H<sub>2</sub>O per pot (about 200 g per ha). With higher rates, nitrogen fixation was only slightly changed. The molybdenum content of the plant tissue rose considerably, however. Since it is a well-known fact that a molybdenum content of the herbage of 20 mg per kg of dry matter may cause cattle-poisoning, care should be taken that these values will not be reached.

With red clover similar results were obtained. Peas and beans did not respond to molybdenum.

In a subsequent pot experiment with 33 soils from different parts of the Netherlands the response of white clover to molybdenum was studied. These soils were mostly rich in iron. On about 20 of these soils big responses to molybdenum were obtained. Amongst the latter soils there were two clay soils.

In another experiment responses to molybdenum in white clover were observed on acid sandy soils with pH-values varying

from 4.2-4.9. The difficulty here was that independently of molybdenum supply, nodulation was much depressed by an acid soil reaction. Once nodules had developed, a clear stimulation of nitrogen fixation was observed when molybdenum had been sup-

plied to the plants.

From these results it may be concluded that molybdenum deficiency is of much more general importance in the Netherlands than was originally believed. No doubt in other countries of Western Europe and perhaps in the U.S.A. similar results may be found. Further research is in progress to study the effect of molybdenum on white clover under field conditions and to see whether other leguminous crops, particularly alfalfa, respond

to molybdenum similarly to white clover.

Another problem which is being studied by the author is the interaction copper-molybdenum. It is a well-known fact that on pastures high in molybdenum cattle will be poisoned by a high molybdenum content in the herbage (teart pastures of Somerset (5)). Under such circumstances copper shows a beneficial effect on the health of the cattle. Burema and Wieringa (4) described an interaction between copper and molybdenum in Azotobacter some years ago. Although in nitrogen fixing white clover in some cases a clear effect of copper on molybdenum supply has been observed by the author, more research has to be done before conclusions can be drawn.

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# COPPER, ZINC, MANGANESE AND MOLYBDENUM DEFICIENCIES IN AUSTRALIA\*

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The aim of this review is to bring before you the circumstances under which trace element deficiencies occur in plants in Australia, and to describe the progress we have made in investigating the problems involved. No reference is made to research done overseas in this field, but that does not imply an

ignorance or a lack of appreciation of it.

Deficiencies of one or more of the elements copper, zinc, molybdenum and manganese are those most important to agriculture in Australia. Corrective treatments are applied to sown pastures and small grain crops over very extensive areas, and commonly to fruit trees and vegetable crops. Moreover, we have discovered the occurrence of various trace element deficiencies, chiefly zinc and copper, in much of the undeveloped country in our higher-rainfall areas. Grain crops and pastures are now being sown in these lands, which were formerly considered useless.

The most common occurrence of these deficiencies is in southern Australia, in regions of winter rainfall and summer drought, where the rainfall exceeds about sixteen inches per annum; or more precisely, south-western Western Australia, south-eastern South Australia, southern Victoria, Tasmania and south-eastern New South Wales. Many thousands of square miles are involved in all, but lest I mislead you I must point out that the country affected in this way represents but a fraction of the total of our agricultural lands.

Certain deficiency diseases of ruminant animals are also of comparatively frequent occurrence. Among them are "enzootic marasmus," a fatal wasting disease of sheep, caused by cobalt deficiency; "enzootic ataxia" of lambs and "falling disease" of cattle, both caused by copper deficiency; and "coast disease" of sheep, caused by a dual deficiency of cobalt and copper. These diseases are restricted largely to southern Australia. On the other hand, "straight steely" wool, which is a manifestation of mild copper deficiency in sheep, has been observed in every State in the Commonwealth.

The research into the cause of these animal diseases renewed our interest in the deficiency diseases of plants. That "grey speck" disease of oats was manganese deficiency disease had long been known, and it had been a common practice to apply copper to fruit trees for the correction of certain disorders.

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Once copper deficiency was known to be involved in "coast disease" in sheep, however, it was a simple matter to apply the discovery to certain problems involving the growth of pastures and cereal crops in the "coasty" areas. Such promising results were obtained that the research was directed to similar problems in other soils, and there soon followed the discovery of a deficiency of zinc, and later molybdenum, in crops and pastures in many of the agricultural areas.

An excellent account of the main climatic features of Australia and the soil zones that are recognized, is to be found in a well-illustrated handbook entitled "The Australian Environment." This deals briefly with many topics relating to Austral-

ian agriculture (C.S.I.R.O. 1949).

### Manganese \*

Manganese deficiency occurs in cereals in South Australia<sup>1</sup> in cereals and occasionally in vegetable crops in Western Australia<sup>2</sup> and in citrus in coastal New South Wales<sup>3</sup>. There is some indication also that additions of manganese, as well as zinc and copper, may benefit certain legumes in recently reclaimed areas of calcareous peat in South Australia (Anderson 1946b). These occurrences of manganese deficiency are restricted to comparatively small and rather well-defined areas, but usually the crops raised are affected seriously unless corrective measures are taken.

The discovery that "grey speck" or "road take-all" of oats was a manganese deficiency disease enabled Samuel & Piper (1928, 1929) to establish the fact that manganese is essential for plant growth. Piper (1941) later showed that a condition in peas, known as "marsh spot," is due to a partial deficiency of

manganese.

Very considerable differences in the susceptibility of various crops to manganese deficiency have been demonstrated in the field and in water-culture. Of the cereals, oats is the most susceptible (Samuel & Piper 1928, 1929; Leeper 1941). Subterranean clover and peas may remain unaffected in soil that produces manganese deficiency in wheat (Adams 1937; Leeper 1947), and many pasture plants and some weeds have been observed to grow well in soils that will not grow healthy oats (Samuel & Piper 1929; Leeper 1935a). There is evidence also of variability among the pasture plants themselves (Anderson 1946b).

The soils that produce crops deficient in manganese are not themselves deficient in that element. The chemistry of man-

4—Samuel & Piper (1928); Piper (1931); Leeper (1935a).

<sup>1—</sup>Samuel & Piper (1928); Piper (1931); Scott (1932). 2—Carne (1927); Teakle, Hoare & Thomas (1933); Wild (1934); Adams (1937); Teakle (1939 and 1945); Teakle & Morgan (1939); Teakle & Wild (1940); Teakle, Morgan & Turton (1941); Teakle & Turton (1943). 3—Levitt & Nicholson (1941); Benton (1942).

ganese in the soil and the factors concerned with its availability are therefore very important, and have received much attention.5 Control methods that are adopted, however, are confined to applications of manganese as a fertilizer and to cultivation of less susceptible crops.6

In oats, the concentration of manganese is highest during the early growth stages. There is not a marked fall as the plants mature, and during grain formation most of the manganese remains in the straw (Piper & Walkley, 1943). It will be seen later that this differs from the behaviour of zinc and copper under the same conditions. Plants showing evidence of manganese deficiency are found to contain much less manganese than healthy plants (Samuel & Piper 1928, 1929), and one of the consequences of the deficiency is an accumulation of nitrate in the tissues (Leeper, 1941).

### COPPER

Copper deficiency in plants is of such widespread occurrence in south-eastern South Australia and south-western Western Australia that it is not possible in a review of this nature to describe the areas and the soils concerned. In general, the deficiency is most common in the sandy and gravelly types, and it is there quite frequently associated with zinc deficiency. On geochemical evidence this is not surprising (Thomas 1938, 1940). Many of these soils are aeolian in origin and have been derived in geologically recent times from calcareous sands (Crocker 1946). It is in areas of the calcareous sands as they exist today that cobalt and copper deficiency in ruminant animals (Marston et al, 1938; Marston, Lee & McDonald 1948a, 1948b; Marston and Lee 1948a, 1948b) and copper deficiency in plants (Riceman & Donald 1938; Riceman, Donald & Evans 1940; Piper 1938) are exhibited in their most acute forms. Zinc deficiency has also been observed there, under certain conditions (Riceman & Anderson 1941; Riceman, unpublished data). Copper deficiency has been observed in other soils, including peats, rendzinas and terra rossas. Over all types the range of soil pH extends from strongly acid to highly alkaline.

The deficiency is of most common occurrence in cereal crops and pasture plants, particularly the pasture legumes. Vege-

<sup>5—</sup>Samuel & Piper (1928, 1929); Piper (1931); Leeper (1934, 1935a, 1935b, 1940, 1947); Leeper & Swaby (1940).
6—Samuel & Piper (1928); Scott (1932); Wild (1934); Adams (1937);
Teakle & Morgan (1939); Teakle & Wild (1940).
7—Piper (1938); Riceman & Donald (1938); Riceman, Donald and Evans

<sup>(1940);</sup> Riceman & Anderson (1943a); Riceman (1945, 1948a); Stewart & Teakle (1939); Teakle & Morgan (1939); Teakle, Turton & Throssell (1940); Teakle, Thomas & Turton (1941); Teakle (1942b, 1943); Teakle & Turton (1943); Beck (1941); Bennetts et al (1941); Strong (1941); Underwood & Beck (1941); Wild & Teakle (1941); Bennetts & Beck (1942); Lee & Riceman (unpublished report, 1943);

table crops are affected in localized areas, mostly in Western Australia, and there are records of the deficiency occurring in fruit trees in some of the fruit-growing areas8

In many localities where sheep produce "steely" wool there are no visible signs of copper deficiency in the plants constituting the deficient diet. This may be a matter of species resistance, but it suggests that copper deficiency could become a limiting factor for other species of plants which might be introduced into those areas.

Fortunately, the prevention or control of copper deficiency in field crops and pastures is usually a simple matter. Most arable soils in southern Australia are deficient in phosphate, necessitating annual applications of superphosphate. Copper sulphate is incorporated in this fertilizer, as required, and is thus distributed with it at little additional cost.

Usually a single application of about 7 lb. of copper sulphate per acre brings about complete control of copper deficiency in both crops and pastures.9 Corrective dressings do not have to be applied annually. In fact, a single light dressing of copper sulphate will prevent the recurrence of copper deficiency in the crops and pastures for many years, even where the deficiency has occurred in its most acute form. 10 As little as 7 lb. of copper sulphate per acre is excessive on some of the sandy soils, and 2 lb. or 3 lb. per acre have proved satisfactory under those conditions (Teakle 1942a; Wild & Teakle 1942; Northcote & Tucker 1948).

Copper deficiency in one of the calcareous sands is extremely acute (Riceman & Donald 1938; Riceman et al 1940; Piper 1938). Copper sulphate applied to that soil at seeding will enable the cereals to produce grain. A further and even a more striking improvement in the crop can be obtained, however, by applying the copper dressing several months before seeding is commenced (Riceman 1946). It appears that the application of copper to this particular soil not only corrects the copper deficiency, but also increases the supply of available nitrogen from the accumulated plant residues and increases the supply of available zinc. In this a time factor is evidently involved, which would also account for the transient nature of the responses observed after applications of zinc to this particular soil (Riceman, unpublished data). In Australian experience this is an exceptional case, al-

Underwood et al (1943); Jones & Elliott (1944); Anderson (1946b); Trumble & Ferres (1946); Bennetts, Beck & Harley (1948); Trumble (1949); Waite Institute Report (1950).

<sup>8—</sup>McCleery (1929); Pittman (1935, 1936); Dunne (1938, 1946); Teakle & Morgan (1939); Teakle, Morgan & Turton (1941); Teakle, Johns and Turton (1943); Teakle & Morgan (1943); Ward (1946).

9—Riceman, Donald & Evans (1940); Riceman & Anderson (1943a); Rice-

man (1945, 1948a); Teakle, Morgan & Turton (1941); Teakle (1942a); Piper (1942); Wild & Teakle (1942); Jones & Elliott (1944).

10—Riceman & Anderson (1943a); Riceman (1948a, 1948b, 1948c); Jones & Elliott (1944); Dunne (1948); Northcote & Tucker (1948).

though it is seemingly not without parallel in other countries. An increase in activity of the soil microorganisms when the copper deficiency is corrected may account for the observed phenomena. This has yet to be proved.

Much attention has been paid to studies of the copper content of plants, chiefly for purposes of diagnosing or confirming the possible occurrence of copper deficiency in crops, pastures and stock. It has become evident that the assimilation of copper is governed to a greater extent by species than by the soils in which they are grown (Riceman, Donald & Evans 1940; Teakle, Thomas & Turton 1941; Piper & Walkley 1943; Moore 1950).

The copper content of cereals is highest during the early growth stages, and declines with increasing age of the plant (Beck 1941; Piper 1942; Piper and Walkley 1943). Applications of copper to the soil bring about very little, if any, increase in the copper content of these plants, even under conditions where copper deficiency is known to be acute (Teakle, Turton & Throssell 1940; Riceman, Donald & Evans 1940; Teakle, Thomas & Turton 1941; Piper 1942; Teakle & Turton 1943). The same is true in respect to potato and tomato plants (Teakle, Morgan & Turton 1941).

Visible symptoms of copper deficiency in wheat, barley and oats are well-defined, particularly so in oats (Piper 1938, 1942; Riceman & Donald 1938; Riceman, Donald & Evans 1940; Riceman & Anderson 1943b; Wild & Teakle 1942; Millikan 1944; Dunne & Throssell 1948). This is fortunate, because a determination of the copper content, except perhaps at the seedling stage, is of little value for diagnostic purposes (Wild & Teakle 1942;

Teakle & Turton 1943; Dunne 1948).

Lucerne, subterranean clover and other legumes, however, can accummulate comparatively large amounts of copper, and the concentration varies considerably according to the soil in which the plants are grown. An application of copper to the soil usually brings about an appreciable increase in the copper content of these legumes (Riceman et al 1940; Teakle, Thomas & Turton 1941; Piper 1942; Teakle & Turton 1943). Analysis of leaf and petiole material has been found to provide useful information in regard to the well-being, not only of the plants themselves, but also of the animals grazing them (Beck 1941; Teakle, Thomas & Turton 1941; Wild & Teakle 1942; Teakle & Turton 1943). This again is fortunate, for it is uncommon to find any visible symptoms of copper deficiency in these species in the field, other than reduced growth and poor seed production (Riceman, Donald & Evans 1940; Riceman 1948a; Strong 1941; Piper 1942; Jones & Elliott 1944).

It would appear that developing floral organs of oats have a higher copper requirement than developing leaves. Comparatively mild copper deficiency leads to death of the flowers during the early stages of development (Wood & Womersley 1946), and in this way inhibits grain production while not causing any

serious hindrance to vegetative growth. In fact, continued vegetative growth, in the form of new tillers, is a characteristic feature of copper-deficient oats (Riceman et all 1940, 1943b; Piper 1942). It is for this reason that a crop already affected by copper deficiency can be made to produce grain even though the application of copper is delayed until quite late in the season (Riceman et al 1940, 1943a; Piper 1042).

In subterranean clover (Riceman 1945, 1948a; Jones & Elliot 1944), in peas (Riceman et al 1938, 1943b; Strong 1941; Teakle, Morgan & Turton 1941; Piper 1942), and in other crops too, a lowered seed production reflects an incipient copper deficiency where vegetative growth is not seriously curtailed.

Approximately half of the copper in maturing oat plants finds its way into the grain (Piper & Walkley 1943), but the immediate source of this copper has not been determined. It is thought that the leaves make no contribution, as there is evidence that all the copper reaching them is immobilized (Wood & Womersley 1946). Continued absorption is not vital to flowering and seed production, because plants grown for only 14 days in water-cultures containing adequate copper and then transferred to cultures that are copper-free, will grow to maturity and produce grain (Piper 1942). There is clearly a need for further research into the distribution of copper among the various parts of the plant, and into the factors concerned with its translocation, particularly translocation into the developing inflorescences.

Wherever copper deficiency has been observed there are records of species and varieties that survive and even flourish in the deficient terrain. A few instances of this so-called "resis-

tance" will serve to show that Australia is no exception.

In certain areas in Western Australia, drooping-flowered clover (Trifolium cernuum), fog grass (Holcus lanatus) and Lotus major persist where subterranean clover fails on account of copper deficiency (Teakle & Morgan 1939: Beck 1941: Jones & Elliott 1944). In South Australia, large tracts of calcareous sand are colonized by two poor-quality grasses (Bromus madritensis and Lagurus ovatus) and occasionally by the native legume Swainsona lessertiifolia. These species grow vigorously and produce a mass of seed, while many cultivated plants will not even survive in that soil unless additional copper is provided (Riceman et al 1938, 1940). Rye corn is a "resistant" crop which can be grown in copper-deficient soils (Riceman et al 1938, 1940; Teakle & Morgan 1939; Piper 1942). Rotenburger black oats and Avena strigosa, two varieties introduced from Europe for experimental purposes because of their reported "resistance" to copper deficiency, have flourished where the cultivated varieties of oats will produce but little grain or none at all (Riceman et al 1940, 1943b). These are all striking examples, but less obvious cases of "resistance" or "susceptibility" are equally common (Teakle & Morgan 1939; Teakle,

Morgan & Turton 1941; Riceman 1945, 1948a; Anderson 1946b). Their occurrence intensifies the need for a better understanding

of the processes of absorption and utilization of copper.

In Western Australia and South Australia good correlation has been obtained between the copper content of pastures and the observed occurrence in ruminant animals of various manifestations of copper deficiency, such as "ataxia" in lambs and "falling disease" in cattle (Beck 1941; Underwood & Beck 1941; Bennetts et al 1941; Bennetts & Beck 1942; Bennetts, Beck & Harley 1948; Marston & Lee 1948b and unpublished data; Lee 1949). However, it is only after detailed studies of this sort have been carried out in the regions concerned, that the copper content of the pasture can be related, with any certainty, to its ability to maintain stock in good health. Due consideration must be given to the influence of growth stage, botanical composition and the extent to which the pasture has been grazed (Beck 1941; Marston & Lee 1948b). Even then there are a number of more elusive factors that can invalidate the conclusions. Among these are seasonal conditions (Lee 1949), exemplified by the rate of growth of the plants, and possibly the molybdenum content of the herbage (Marston & Lee 1948b and unpublished data; Marston 1949; Bull 1949), which itself varies independently of the copper content (Piper & Beckwith 1949; Moore 1950).

### ZINC

Zinc deficiency has been observed in pastures<sup>11</sup> and cereal crops<sup>12</sup> in Western Australia, South Australia and Victoria. It is most common, but by no means universal, in soils of light texture, and in those soils it is often associated with copper deficiency. Zinc deficiency has also been observed in flax in very restricted areas of heavy soil (Adam & Piper 1944; Millikan

1946, 1947a; Cass Smith & Harvey 1948).

In Western Australia and in South Australia a disorder known as "rosetting" occurs in pine trees in sandy soil (Kessell & Stoate 1938; Teakle 1939; Teakle & Turton 1943; Stephens et al 1941; Northcote & Tucker 1948). In all States there are records of either "little-leaf" in deciduous fruit trees (Morwood 1937; Ward 1939, 1944; Anon. 1944; Kemp & Beare 1944; Kemp 1946; Walsh 1948; Wade 1949b; Gayford 1949) or "mottle-leaf" in citrus (Pittman & Owen 1936; Benton 1937, 1942; Strickland 1937; West 1938; Teakle 1939; Anon. 1943, 1944; Gayford 1947). All three disorders are the result of zinc deficiency.

12—Millikan (1938, 1940, 1941); Forster & Hore (1939); Riceman & Anderson (1941, 1943a); Riceman (1945, 1946); Dunne & Throssell (1948); Dunne, Smith & Cariss (1949); Anon. (1949a).

<sup>11—</sup>Riceman & Anderson (1941, 1943a); Riceman & Powrie (1948); Riceman (1945, 1948a, 1950); Ferres & Trumble (1943); Teakle & Turton (1943); Anderson (1946); Trumble & Ferres (1946); Waite Institute Report (1950).

By means of water-cultures it has been possible to produce well-defined symptoms of zinc deficiency in cereals (Piper 1940b; Millikan 1942) and in flax (Millikan 1942). In field grown cereals, however, the symptoms are not always well-defined, even where the deficiency is comparatively acute (Millikan 1938, 1942; Forster & Hore 1939; Riceman & Anderson 1843b; Dunne & Throssell 1948). On the other hand, oats grown in recently cleared sandy soil commonly develop a striking bronze discolouration, particularly in the lowest leaves (Riceman 1945; Dunne, Smith & Cariss 1949). Such a pronounced discolouration is not one of the accepted symptoms of zinc deficiency and may be due to complications involving phosphorus. It is corrected by an application of zinc sulphate which also increases the grain yield considerably.

The productiveness of subterranean clover, which is the legume most commonly employed in pastures in these light soils, can often be increased strikingly by an application of zinc sulphate. In these situations it is usually necessary to apply copper as well, to improve the production of seed (Riceman 1945, 1948a). The appearance of the plants may give no indication at all of zinc deficiency, except in relatively acute cases, when dwarfing and yellowing of the leaves and failure of the stems to elongate provide unmistakable evidence of zinc deficiency (Ferres, personal communication; Powrie & Riceman, unpublished data).

Trial and error methods in the field, using appropriate fertilizers, are thus still indispensable in determining the need for applications of zinc where the deficiency is suspected. Similar methods, carried out in small pots of the suspected soils in the glasshouse, prove a useful subsidiary to investigations in the field (Ferres & Trumble 1943).

Some progress has been made in efforts to recognize incipient zinc deficiency in subterranean clover by means of plant analysis. Legumes accumulate more zinc than grasses grown in the same soil (Piper & Walkley 1943), and their zinc content varies widely according to growth stage, soil, and fertilizer treatment (Teakle & Turton 1943; Riceman, Powrie & Jones, unpublished data). The determination of the zinc content of leaf and petiole material of subterranean clover, collected at the time of flowering, seems to show promise of revealing incipient zinc deficiency in these plants (Teakle & Turton 1943; Riceman, Powrie & Jones, unpublished data). However, such data must still be interpreted with reserve because light duration, air temperature, and other environmental factors can influence the uptake of zinc and its distribution within the plant, often with far-reaching consequences (Trumble & Ferres 1946; Ferres 1949).

Some attention has been paid to the distribution of zinc in oats and to the effects of inadequate absorption, but similar studies in subterranean clover have been sadly neglected.

In oats the concentration of zinc is highest during the seedling stages (Piper & Walkley 1943) but absorption continues throughout the growing period (Sibly 1949). At maturity, about three-quarters of the zinc in the above-ground parts of the plant is concentrated in the grain (Piper & Walkley loc. cit.). It appears that the leaves do not contribute to this concentration, as all the zinc reaching the leaves is retained permanently by them, even under conditions of zinc deficiency (Sibly loc. cit.).

There is some evidence that zinc is involved in phosphorus metabolism (Quinlan Watson, private communication), in protein synthesis (Sibly 1949) and in the rate of photosynthesis (Ferres 1949), of plants.

In preliminary investigations into the relation of zinc to phosphorus metabolism, zinc-deficient oats in water-cultures were found to contain extremely large amounts of phosphorus, of which an abnormally large proportion was in the inorganic form (Quinlan Watson, private communication). The ratio of P to Zn, at the late tillering stage, was not below 1000:1 and in some cases it greatly exceeded that figure. The ratio in zinctreated plants was of the order of 300:1. A ratio of 100:1 (P<sub>2</sub>O<sub>5</sub>/ Zn ratio of 230) has been observed at maturity in wheat grown on fertile soil (Walkley 1940). Further research in this direction is justified on practical as well as on theoretical grounds. If an abnormal accumulation of phosphorus proves to be a general consequence of zinc deficiency, the ratio of P to Zn would give a clear indication of deranged metabolism. This ratio, by varying more widely than the simple concentration of zinc, would assist in determining whether observed values for zinc content at any particular growth stage represent "sub-optimal" concentrations.

Heavy applications of superphosphate have been observed to induce or to intensify symptoms of zinc deficiency in citrus (West 1938), flax (Millikan 1946, 1947a; Cass Smith & Harvey 1948), oats (Riceman 1945), and subterranean clover (Powrie & Riceman, unpublished data), but no attempt has been made to determine the mechanism by which this is brought about. It may be significant that all these species are rather susceptible to zinc deficiency (Forster & Hore 1939; Millikan 1942; Adam & Piper 1944; Riceman 1945, 1948a; Trumble & Ferres 1946), and that lucerne, which is remarkably resistant to this deficiciency (Riceman 1945, 1948a; Anderson 1946b; Trumble & Ferres 1946), flourishes where dressings of superphosphate as high as 8 cwt. per acre are applied without any zinc supplement (Riceman 1948a; Riceman & Powrie, unpublished data). At the other end of the scale, certain weeds, notably Fumaria officinalis, will tolerate a concentration of zinc that is too high for flax (Millikan 1947b).

It is fortunate that zinc deficiency in susceptible crops and pasture species can be prevented by relatively light dressings of zinc sulphate. Quantities as low as 5 to 14 lb. per acre are applied to cereals and pastures in peat and light soils (Riceman 1945, 1948a, 1950; Anderson 1946b; Dunne, Smith & Cariss 1949; Waite Institute Report 1950), while 15 to 30 lb. is adequate for flax and cereals grown in soils of heavier texture (Millikan 1938, 1941, 1946; Forster & Hore 1939; Adam & Piper 1944; Cass Smith & Harvey 1948). One single application of a dressing as light as these is sufficient to protect the crops and pastures from zinc deficiency for many years. In this regard it is interesting to find that the quantity of zinc added inadvertantly to these soils may amount to the equivalent of 1/4 to 1/2 lb. of zinc sulphate for every 1 cwt. of superphosphate that is applied (Walkley 1940; Oertel and Stace 1947; Dunne & Throssell 1948). This is sufficient to replace most, if not all, of the zinc removed by a high yielding wheat crop (Walkley 1940). Such small quantities of zinc may be of no consequence in the initial prevention of zinc deficiency in crops and pastures in zinc-deficient soil (Walkley loc. cit.; Powrie & Riceman, unpublished data), but their regular addition as an impurity in superphosphate probably delays the need for further deliberate applications of zinc.

### MOLYBDENUM

It is not long since molybdenum was first discovered to be a limiting factor in the growth of legumes in certain acid soils in South Australia (Anderson 1942). The discovery stimulated a search for the existence of a similar condition elsewhere. There are reports now of molybdenum deficiency in pasture legumes, chiefly subterranean clover and lucerne, in several other States, and further occurrences have been observed in South Australia (Fricke 1943, 1944, 1945a, 1945b; Stephens & Oertel 1943; Shaw, Barrie & Kipps 1944; Teakle 1944; Trumble 1945; Trumble & Ferres 1946; Anderson 1946a, 1948; Anderson & Spencer 1949; Northcote & Tucker 1948). In Tasmania, a disease in oats known as "Blue Chaff" has been controlled by applications of molybdenum (Fricke 1947). Reference will be made later to the occurrence of molybdenum deficiency which is thought to be associated with manganese toxicity.

New Zealand work provided the clue to the cause of "Whiptail" disease in cauliflowers, and dressings of molybdenum are now commonly used in vegetable-growing areas in Australia to control not only "Whiptail" (Waring, Shirlow & Wilson 1947; Wilson & Waring 1948; Waring, Wilson & Shirlow 1948, 1949; Dunne & Jones 1948; Wade 1949a), but diseases in a number of other crops as well (Fricke 1944, 1945a; Wilson 1948, 1949a,

1949b; Anon. 1949a).

The molybdenum deficiency diseases are, with few exceptions, confined to plants growing in soils having an acid reaction. Dressings of lime, wood ash, or other alkaline material are usually effective in alleviating the condition and were commonly

used before it was suspected that molybdenum was involved (Anderson 1942, 1946a; Anderson & Oertel 1946; Stephens & Oertel 1943; Waring, Wilson & Shirlow 1948, 1949). It is now known that the benefit of these dressings can be attributed to their influence on molybdenum availability (Oertel, Prescott & Stephens 1946).

Effective control of the deficiency is obtained by direct applications of molybdenum to the soil. The quantities applied are extremely small. No more than 1 to 2 oz. of molybdenum trioxide per acre are required to give complete control of the deficiency in subterranean clover (Anderson 1946a, 1948). Rather heavier dressings, mostly in the form of ammonium molybdate or sodium molybdate, are applied to vegetable crops (Waring, Shirlow & Wilson 1947; Waring, Wilson & Shirlow 1948, 1949).

A spectrochemical survey of phosphate rocks of different origin, and of superphosphate made from them, has revealed differences in the amount of molybdenum present (Oertel & Stace 1947). No molybdenum was detected in rock from Nauru and Ocean Island, where Australia's supplies are normally procured, but rock from Egypt, Algeria and Florida contained traces of molybdenum amounting to several parts per million. The superior results that are occasionally obtained in molybdenum-deficient areas with some superphosphates may be due to this impurity (Trumble & Ferres 1946; Millikan 1948-1949), since it is known that deliberate applications of as little as 1/16 oz. of molybdenum trioxide per acre to deficient soil can exert a beneficial effect on the growth of subterranean clover (Anderson 1946a).

The restricted growth of subterranean clover plants in molybdenum-deficient soils is due to nitrogen deficiency in the host-plant, brought about by a breakdown in the process of symbiotic nitrogen fixation (Anderson 1946a, 1948; Anderson & Thomas 1946; Anderson & Oertel 1946; Anderson & Spencer 1949). The host-plants are not directly affected by the molybdenum deficiency. They respond vigorously to dressings of nitrogen fertilizer where no molybdenum is added. Grasses behave similarly.

Subterranean clover grown in the affected soils may not derive full benefit from applications of molybdenum unless the plants are adequately manured with phosphate (Anderson 1946a). In this the host-plant is concerned directly (Anderson & Thomas 1946; Anderson & Oertel 1946). A parallel case has been discovered where sulphur deficiency inhibits a molybdenum response by subterranean clover. The nitrogen metabolism of the host-plant, in this case, is limited directly through lack of sulphur, while symbiotic nitrogen fixation is limited through lack of molybdenum (Anderson & Spencer 1949).

The concentration of molybdenum in healthy plants of lucerne and subterranean clover is found to be extremely low; it seems that a concentration of not more than 1 part of molybdenum per 10 million of dry weight of leaf and stem is adequate

for normal metabolism of the host-plant (Teakle 1944; Anderson & Oertel 1946; Oertel, Prescott and Stephens 1946). In these species, and in several other legumes that have been examined, more molybdenum is found in the roots than in the tops, and much more is found in the nodules than in the tissues of the root itself (Jensen and Betty 1943).

In crops that are affected directly by molybdenum deficiency, such as vegetable crops, nitrogen metabolism is upset and this leads to an accumulation of nitrate in the tissues and to the development of pronounced lesions on the leaves (Piper 1940a; Fricke 1947; Wilson & Waring 1948).

In some soils, molybdenum deficiency is associated with manganese toxicity. This has been observed in subterranean clover (Anderson 1948), in beans (Wilson 1949a), and in flax (Millikan 1948-1949). Addition of molybdenum appears to alleviate the condition by producing some measure of tolerance to the high concentrations of manganese. This is supported by laboratory investigations, which have demonstrated an effect of molybdenum in reducing the symptoms of toxicity induced in flax by high concentrations of manganese and several other heavy metals (Millikan 1947c, 1948, 1949).

### FUTURE TREND

From this review it will be evident that research into the trace element deficiencies in Australia has been directed very largely to the solution of the immediate problems of prevention or control. Rapid progress has been made during the past decade, but further advances are becoming ever more dependent upon an extension of basic knowledge. For this it is no longer sufficient for us to depend upon our colleagues overseas, and so in Australia now the emphasis in research is shifting from the practical to the fundamental aspect of nutrition, and the species under observation are the ones most commonly employed in our own deficient terrain.

Such a change in the direction in which research progresses is naturally a slow one, but in the future we may hope to see advances that will enable us to comprehend more clearly the

true significance of our experimental findings.

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# THE SIGNIFICANCE OF TRACE ELEMENTS IN RELATION TO HEALTH OF RUMINANTS IN GREAT BRITAIN\*

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The purpose of the present paper is to provide a brief review of the significance of the so-called "trace elements" or "minor elements" in relation to disorders of ruminants as they occur in Great Britain, in comparison with occurrence of similar disorders in other parts of the world.

Pigs and poultry are omitted from consideration, partly because of differences in requirements of animal species, partly because so much of the food in their mixed rations is imported and not characteristic of any one farm, and partly because of the occurrence of minor elements in the mineral mixtures normally fed to them to ensure adequate intake of major elements. At any rate, they do not seem to present the definite regional problems characteristic of ruminants restricted to pasture and supplementary foods grown on single farms or definite geographical areas.

As well known to all agricultural chemists and physiologists, the number of minor elements found in plant and animal tissues is very large, and traces of almost any element present in soils can appear in a plant simply because they are brought into solution by the action of its roots and can not be entirely re-Some of these are inert, like nickel, which is always present in soil grown vegetation but without which the plant grows equally well in water cultures from which the element is carefully excluded, and upon which no known physiological process of the consuming animal is known to depend. Others, such as boron, are essential for plant health and hence find their way into animal tissues where, however, they are not known to serve any useful purpose. A third group, exemplified by selenium, serve no useful purpose either in plants or animals but can be tolerated by certain species of plants in such large quantities that they cause "selenosis" (the old "alkali disease" of South Dakota) in animals consuming them.

The "trace elements" only become economically important if they happen to be essential micro-nutrients, the absence of which causes "deficiency disease," or if they occur in soils in excessive amounts injurious to plants or animals, or if they appear as the result of contamination by industrial processes.

It is proposed to limit consideration to manganese, iodine,

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cobalt and copper, as examples of essential micro-nutrients, molybdenum as example of a minor element important in Great Britain when present in pastures in injurious amounts, and fluorine as example of a minor element which has come into prominence in recent years through industrial contamination of pastures grazed by ruminants.

### MANGANESE

This element is mentioned only because of prevalent misconceptions concerning its importance. Although it is an essential micro-nutrient in animal life and, on the basis of experimental work on rats it is believed to affect growth rate, skeletal metabolism, ovulation and development of the foetus, when the adequate traces are not available, it is usually present in sufficient amounts in the vegetative parts of plants to cover the requirements of grass-eating animals. This is true even when soil conditions are such as to lead to definite symptoms of manganese deficiency in susceptible plants, and it is not uncommon to see signs of manganese deficiency in oats, wheat and peas grown on cultivated soil, when adjoining similar soil under grass is carrying perfectly healthy cows showing none of the signs of manganese deficiency which would be expected from the known effects of experimentally induced deficiency in small laboratory animals.

Some years ago the view was put forward by Hignett (1941) in Britain that a form of delayed ovulation in the larger farm animals, when the female comes into heat and accepts the male before descent of the ovum, could be attributed to manganese deficiency of pasture occasioned by excessive liming of the soil. Subsequent investigation, however, involving attempts to control the temporary infertility by manganese therapy, has not substantiated the view and it has been abandoned by Hignett himself.

The converse case of possibly injurious effects of high manganese in pastures can also be dismissed as highly improbable. An earlier suggestion (Blackmore et al. 1937) that high manganese was conducive to hypomagnesaemic tetany failed to find corroboration in experimental observations of Allcroft (1937),

and has not stood the test of time.

#### IODINE

It is hardly necessary to mention that iodine is required for the formation of thyroxine, the hormone of the thyroid gland, and that goitre is the common sign of dietary deficiency. Daily animal requirements are small, however, and traces of the order 0.05 mg.-0.10 mg. per 100 lb. body-weight are sufficient. Nevertheless, acute iodine deficiency occurs in farm stock in many parts of the world, manifested as congenital thyroid hyperplasia in piglings, calves and lambs, and less commonly as goitre in adult cattle, sheep, goats and pigs. It should be emphasized, however, that direct iodine deficiency in the food is not the only cause of thyroid hyperplasia, and that any factor which reduces absorption of iodine, or increases the utilization of thyroid hormone, may increase normal demand, and that substances may be present in plants which interfere with the proper metabolism of the thyroid gland itself.

In Great Britain typical iodine deficiency in farm stock is very rare, but has been recorded in both lambs and calves, notably by Jamieson *et al.* (1945 and 1947) and associated with charac-

teristically low iodine content of the thyroid gland.

The type of "conditioned iodine deficiency" brought about by some "goitrogenic factor" in the food is also recognized, and an extreme case of naturally occurring congenital thyroid hyperplasia in lambs, resulting from excessive feeding of kale to pregnant ewes, may be cited (Shand & Allcroft 1950). The outbreak occurred in the spring of 1949 in a flock of 500 Oxford cross-bred ewes in Nottinghamshire, many of which delivered still-born lambs or lambs which died a few minutes after birth, showing notable thyroid hyperplasia. Associated with this was the fact that the kale crop had been exceptionally good and provided the major ration during the gestation period. suggested the "goitrogenic factor" known to be present in cabbage and it was decided to attempt to reproduce the condition experimentally the following year. The main flock fed under ordinary farm management on roots, grass and hay, was limited to a small amount of kale and, to protect the farmer in case genuine iodine deficiency was involved, was hand-dosed at fortnightly intervals with potassium iodide. Two groups of 50 each, however, were isolated for experimental purposes, one fed on the same ration as the main flock but without the supplementary iodine and the other fed exclusively on kale from tupping time until lambing. The kale supply, and practical difficulty of isolating a third group, prevented inclusion of a trial with "kale only plus iodine" but the limited results dramatically established kale as the causal factor. The lot fed roots, hay, and limited kale, lambed normally with an average of three lambs for every two ewes. The lot fed exclusively on kale averaged less than one surviving lamb for every two ewes. Some of the ewes aborted and of the lambs which were born alive a large proportion died within a few hours with enlarged thyroid glands, the largest of which weighed 270 grams. Iodine determinations on blood of the ewes at intervals during gestation showed no difference in total iodine and protein-bound iodine, as between those fed exclusively on kale and those fed on limited kale, although the ewes of the main flock receiving iodine showed, as would be expected, much higher values. Iodine values on all the enlarged thyroid glands of the lambs in the kale group were low although not all as low as was expected. The experiment is being repeated for 1950-1951, including an iodine supplement to a

kale fed group, but provisionally it is anticipated that iodine may not act prophylactically. The clinical condition in the lambs did not suggest low iodine goitre as known in iodine deficient areas, but rather suggested an anti-thyroxin factor interfering with the metabolism of the gland in spite of adequate iodine intake. Even those lambs with only moderate thyroid hyperplasia, and which could have been expected to survive, died on the day of birth, often within a few minutes of delivery. Few of the ewes themselves showed any obvious abnormality—thyroid enlargement in this case was not palpable except in one or two instances.

#### COBALT

There is no need to recapitulate the classical work on cobalt deficiency in Australia and New Zealand, where occurrence was on the grand scale in some areas until the etiology of various obscure conditions was cleared up by the work of Underwood

and Filmer (1935) and of Marston and Lines (1935).

In Great Britain "enzootic marasmus" of cattle does not appear to have been specifically recorded except on the Isle of Tiree in the Hebrides, but subdued cobalt deficiency doubtless exists in cattle in areas where "pine" of lambs is well established. In Scotland, "pining" or "vinquish" in lambs has been known as a debilitating disease from time immemorial, was attributed to iron deficiency in the late twenties, and definitely shown to be due to lack of cobalt in 1938 (Corner and Smith, 1938) when Australian work became well known. Since that date the most valuable work in Scotland has been done by collaboration between the Macauley Institute for Soil Research in Aberdeen and the Moredun Institute of the Animal Diseases Research Association at Edinburgh. A map of the affected areas was given by Stewart, Mitchell and Stewart (1946) and further investigation is rapidly adding to its scope and accuracy. Large tracts of land north of Inverness are affected, and specific districts in the Solway area and Roxburghshire in the south have been defined. In England the areas most definitely affected are the granite and sandstone soils of Devon and Cornwall investigated by Patterson (1946).

Other areas of Great Britain are also affected to a lesser extent and forms of subdued cobalt deficiency have been reported from the Northern Counties in England, from the Fens of Norfolk, and hill lands of Wales, but no systematic mapping has yet been undertaken and the true position is uncertain. It has been suspected but not yet investigated in Ireland, on soil formation similar to those of affected areas in England and Scotland.

In general the course of investigation has followed the lines of Australasian work very closely and the method of dealing with the problem is much the same. Where pastures are under proper management fertilization of the soil with the requisite small quantities of a cobalt salt is the simplest procedure. The Scottish workers favour an application of 2 lb. per acre of cobalt sulphate once in a rotational course of four years, as compared with the annual application of 5 oz. per acre favoured in New Zealand. Where the value of the land does not repay systematic pasture management as with much of the rough hill grazing in various parts of affected country, reliance is placed on suitable mineral mixtures offered ad libitum or on oral dosing as often as the shepherd can manage it.

The safe lower limit for cobalt in pastures in Britain is taken as about 0.08 p.p.m. on the dry matter and it is considered highly unlikely that healthy lambs can be reared on pastures containing less than 0.05 p.p.m. It will be noted that these figures are very similar to those derived from Australia and New Zealand.

Since it is often difficult to secure pasture samples free from a degree of soil contamination which may invalidate analytical results, the Macaulay Institute in Aberdeen prefers soil analyses for survey purposes. Figures for total soil cobalt have little significance but the moiety extractable with 2.5 per cent acetic acid is regarded as a fairly reliable index. The range 0.25-0.30 p.p.m. for acetic-soluble soil cobalt is treated as critical.

The function of cobalt in the animal economy is still obscure. but the fact that naturally occurring cobalt deficiency diseases are confined to ruminants, and are unknown in non-ruminants, at once suggests a functional relationship. That the rumen is specifically involved was indicated by an observation of Marston in Australia about 1940 (not published until later), to the effect that cobalt administered by mouth to cobalt deficient sheep was vastly more effective than cobalt administered intravenously. The reason for this behaviour has been under investigation at the Rowett Institute in Aberdeen, the most recent observations being those of Phillipson and Mitchell (1950). These workers maintained lambs in a cobalt deficient state on a ration of cobalt low hay, flaked maize and maize gluten meal supplemented with cod-liver oil and bone flour, and found that 0.1 mg. Co per day was sufficient to allow normal increase in weight, but that the same daily dose by intravenous injection had no effect, although it led to liver storage of the element. Using various fistulae cobalt was introduced separately into the rumen, abomasum, and duodenum. Good responses were obtained, rather variable in the case of duodenal introduction, but the rumen liquor of all the treated animals contained more cobalt than that of the controls, indicating a backward leak vitiating deductions. They concluded that their observations support the suggestion of Marston and Lee (1949) but do not exclude the possibility that free cobalt is necessary in the abomasum itself.

## MOLYBDENUM

British pastures may be regarded as containing a common normal of about 1 p.p.m.-3 p.p.m. Mo expressed on the dry mat-

ter, and this level is regarded as beneficial. Normal traces are certainly important for fixation of atmospheric nitrogen by free-living Azotobacter in soils and the nodule bacteria of legumes, and Mulder (1948) has assigned a specific function to molybdenum in the nitrogen metabolism of the plant. The lower limits of molybdenum in British pastures have been little investigated, and it is not known whether traces of this element are essential to animals or not, but it is quite certain that it can be taken up from some soils in such excessive amounts that it becomes harmful to grazing ruminants.

The clearest cases of "molybdenosis" occur on the so-called "teart" soils, derived from the molybdeniferous lower lias geological formation in Somerset. Although the association of "teart" pastures with a "scouring disease" of ruminants had been recognized for centuries it was not until about 10 years ago that the explanation was found by workers at Jealott's Hill (Ferguson, Lewis and Watson 1943) and prophylactic measures devised. The disorder mainly affects cows in milk and young stock. Sheep are less affected and horses not at all. Diarrhoea may commence even within 24 hours of putting cattle on to affected pastures in Spring, and the dung soon becomes watery, evil-smelling, and yellow-green in colour. The animals become filthy, develop staring discoloured coats (not true "depigmentation" of hair fibres) and lose condition rapidly, eventually suffering permanent injury or death. The rapidity with which recovery ensues on transfer to non-teart pastures is very characteristic.

The area concerned in central Somerset comprises about 20,000 acres and smaller areas are found in North Somerset, Gloucester and Warwick. So far as is known the problem is negligible in other areas of Britain. The pastures of non-teart areas in the same county are usually below 3-5 p.p.m. Mo (D.M. basis), and rarely exceed 5-7 p.p.m., although occasional values as high as 9-11 p.p.m., and rarer values as high as 20 p.p.m. appear in various parts of Britain. But in the Somerset "teart pastures" figures up to 100 p.p.m. are encountered and figures well above 20 p.p.m. are common. The severity of scouring is directly related to the water-soluble molybdenum in the grass, which is highest during the active phase of growth and lowest in old grass. Diarrhoea, therefore, usually commences in May and ends in October.

The disease is a straightforward "molybdenosis" and can be produced in a few days in stalled animals by dosing with sodium molybdate, on a ration not itself conducive to constipation, or by putting cattle on any growing pasture dressed with molybdate in amount sufficient to bring the molybdenum content up to "teart" levels. The mechanism of the scouring effect is not yet understood but it concerns only the alimentary tract, and the diarrhoea can be controlled by the therapeutic use of copper sulphate, a procedure well known in veterinary practice for most forms of scouring, even those of bacterial origin. A daily dose of 1 gm. for young stock and 2 gm. for cows, administered most conveniently as ½ lb or 1 lb of "anti-teart cake" (copperised dairy cubes) is sufficient to enable the grass to be used right throughout the season. This has little or no effect on the absorption of molybdenum and levels of this element in the blood and urine of the cattle remain high without apparent adverse effect. In "teart" areas the severity of the disease can also be mitigated by cultural procedures or the land used for controlled purposes other than grazing. Legumes absorb more molybdenum from the soil than grasses. Little absorption occurs on acid soils, but on alkaline or neutral soils uptake by plants is rapid. Animals in very good condition on supplementary feeding for milk production seem less prone to scouring at grass than animals limited entirely to high molybdenum pastures.

At first this English "teart" area seemed to represent a geological curiosity, but a few years later Britton and Goss (1946) reported a disease in California resembling "teart" and have since (personal communication) found pasture levels of

molybdenum even higher than those in Somerset.

Of interest also is a case of "industrial molybdenosis" now under investigation near Glossop in England. The factory concerned produces various alloys, mainly special steels, and uses large amounts of molybdenum. Some of this escapes with the chimney effluents and contaminates pastures in the direction of the prevailing wind. Scouring of grazing dairy cows ensues and typical "teart" appears.

Fluorine compounds are also emitted and the clinical picture is one of molybdenosis, hypocupraemia, and mild fluorosis.

## COPPER

Although evidence of copper deficiency in live-stock seems to have been first supplied from Florida in 1931 and Holland in 1933, the most valuable work over the ensuing years has come from Australia. It was not until 1938 that copper was definitely associated with disease in sheep in Britain and not until 1946 that hypocupraemic disorders of cattle came under observation.

Several complex clinical conditions associated with low copper status are now recognized in England, Scotland, Wales, and Ireland, nearly all on pastures normal in copper content. The very low pasture copper levels recorded in some parts of the world, 3 p.p.m. or less, have not yet been observed in Britain and it is believed that "straight copper deficiency" in ruminants does not occur; that recognized disorders associated with hypocupraemia and low liver copper are all "conditioned"; and that there may be a variety of conditioning factors different in character.

Sheep

The disease 'neonatal ataxia of lambs' has a wide geographi-

cal distribution throughout England, Wales and Scotland, but has not so far been reported from Ireland although the occurrence there of hypocupraemic disorders in cattle (Senior 1950) would suggest that this disorder of sheep also occurs in some areas. It has been known for many years in Britain under a variety of names, such as "swayback," "swingback," and "warfa," and has been shown to be pathologically similar to "enzootic ataxia" of lambs in Australia as described by Bennetts and his colleagues (Bennetts and Chapman, 1937; Bennetts and Beck, 1942), and to "renguerra" in Peru described by Gaiger (1917).

Although the disease has a wide distribution throughout Britain, the incidence varies from year to year on the same farms and in the same districts, but there are some areas, notably parts of Derbyshire, where it occurs year after year, the only variation being the percentage of lambs affected each year. Before prophylactic measures were taken the mortality in severely affected areas varied annually from 5 to 50 per cent of the lambs born. Ewes of any age or breed may give birth to ataxic lambs, and ewes which produce affected lambs one year, may produce normal lambs the next, but in our experience occurrence of the disease is broadly related to length of sojourn on 'affected' farms. Observations made in Derbyshire over a period of six years showed that no ewe which had been on an 'affected' farm for less than  $1\frac{1}{2}$  years gave birth to an ataxic lamb.

There appears to be two types of the disease, the common acute form in which the lambs are clinically affected when born, and a 'delayed' type in which clinical signs may develop as late as three months after birth. In both, however, the symptoms are essentially those of a spastic paralysis, particularly of the hind limbs, and vary only in severity. All cases show inco-ordination of movement; severe cases are unable to stand; others may walk with difficulty, sway and tumble. Mild cases show only slight weakness of the hind quarters, particularly when made to move quickly. Severely affected lambs usually die shortly after birth but mild cases often survive, and when bred from later may produce normal lambs. Mothers of affected lambs remain apparently healthy and show no clinical symptoms. No evidence of anaemia associated with low blood status has been observed in Britain, the condition in this respect differing from that in Australia. Innes (1934-35) carried out a detailed pathological study of the disease in England and showed that it is characterized by a diffuse symmetrical demyelination of the cerebrum, varying in extent from small foci in the centrum ovale to gross demyelination of the whole hemispheres with liquefaction and cavitation in extreme cases. Secondary degeneration of the motor tracts in the cord is always present. Fig. 1 gives some idea of the brain lesions. It shows three horizontal sections; the top one is from a normal lamb; the bottom one shows the gross destruction of white matter with extensive cavitation; the middle section shows less severe cavitation.

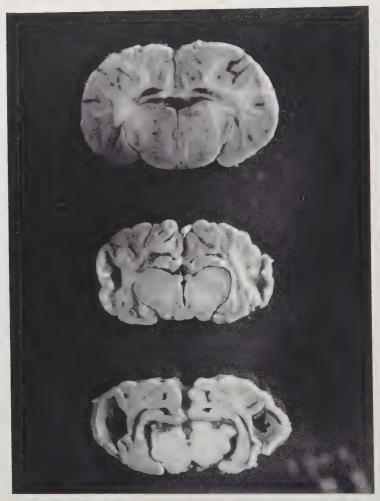


Figure 1.—The various brain sections give some idea of the lesions produced by "Swayback" of sheep in this important organ. The top one is from a normal lamb; the bottom one shows gross destruction of white matter with extensive cavitation; the middle one shows less severe cavitation.

Evidence at present indicates that demyelination occurs at a relatively late stage of gestation, probably within the last six weeks, i.e. after cerebral myelination has begun. Romanes (1947) has shown that the first myelin appears in the forebrain of the foetus at 96 days.

Since the pioneer work of Bennetts and his colleagues it has been well known that the disease is associated with a low copper status of both ewes and lambs and that it can be prevented by administration of copper to the ewe during late pregnancy. Al-

though not feasible in ordinary farming practice, Weybridge work has shown that a single intravenous injection of 20 mg. Cu as copper sulphate to the mother about six weeks before parturition, will also prevent the disease. Sufficient copper is stored in the liver to tide over the intervening period. Although blood copper values of ewes in areas where the disorder is likely to occur are low, commonly about one-third normal, this is of little value for diagnostic purposes since a ewe with a value only one-tenth normal may still deliver a healthy lamb, and sometimes one twin lamb may show the disease and the other not. All that can be said is that if the blood-copper status of a flock is very low the incidence of 'swayback' in the lamb crop is likely to be high, and that if this low status is elevated by administration of copper the disease will vanish. Our own investigations in Derbyshire showed that 'swayback' could occur if the blood copper of the ewe before lambing fell below 0.06 mg/100 ml., and quite frequently occurred at 0.04 mg./100 ml., but nevertheless occurred in only 14 per cent of those ewes with a blood Cu of less than 0.02 mg./100 ml. This indicates that the copper content of the circulating blood of the ewe is not the sole factor determining the incidence of 'swayback' in the lamb, and that shortage of copper supply to the foetus may not be the sole cause of demyelination during late gestation.

Although 'swayback' of Britain and enzootic ataxia of Australia correspond very closely, there is the important aetiological difference that in Australia the disease occurs on pastures low in copper, below 5 p.p.m. on a dry matter basis and commonly below 3 p.p.m., whereas in Britain it occurs irrespective of copper content and is prevalent in Derbyshire at levels of 7 to 15 p.p.m. or more. In Australia the disease has been attributed to a simple copper deficiency rectifiable by fertilizing the soil with copper salts. In Britain another factor seems to operate, which either depresses the availability of the copper in the plant, or in some way interferes with copper metabolism in the animal itself.

The factor in the pastures which induces the disease in spite of normal or high copper content is unknown, but experimental work carried out at Weybridge about 7 years ago showed that it exists in transportable form. From one farm in Derbyshire showing an average of 15 p.p.m. Cu in the pasture dry matter, 20 ewes, each with low blood copper and each with a past history of bearing 'swayback' lambs, were transferred to Weybridge soon after tupping and there fed in stalls on a ration of oats and straw containing only 5 p.p.m. Cu. The blood copper rose rapidly and all lambs were born normal. In the control group left on the farm, with much higher daily intake of copper, blood values remained low and incidence of 'swayback' was 20 per cent. The following year 20 similar ewes were transferred from the same farm along with farm hay to serve as roughage in the Weybridge ration. This time the blood copper remained low and 4

'swayback' lambs were obtained, an incidence of 20 per cent similar to that amongst the controls on the Derbyshire farm in the same year.

There has been much speculation regarding the nature of the unknown factor. Lead has been suggested but the available evidence is against that view. Many 'swayback' pastures are quite normal in lead content and observations at Weybridge showed that a daily dose of 50 mg. Pb as the acetate to hypocupraemic ewes did not increase the incidence of ataxia in the lambs, nor did a high lead intake produce hypocupraemia in normal sheep even when given in quantities ranging from 100 to 400 mg Pb daily for as long as twelve months.

Dick and Bull (1945) and Cunningham (1946) suggested that a high molybdenum content of the grazing might explain the anomaly of a low copper status in ewes and the occurrence of neonatal ataxia in lambs on pastures which show normal copper content, but our own investigations are not in accord with these views and indicate that molybdenum content of pastures in Britain bears no relationship to incidence of swayback. Herbage samples from farms in Derbyshire where incidence of swayback was high showed normal molybdenum values of 0.6 to 1.8 p.p.m. on dry matter, while on certain farms in the teart area of Somerset swayback is unknown on pastures with molybdenum

contents ranging from 15 to 40 p.p.m.

Since the unknown factor need not be inorganic, but might be an organic compound competing for copper in enzyme systems in the same way as 2, 3-dimercaptopropanol (B.A.L.) competes for certain metals when used as a detoxicating agent, large daily intramuscular injections of this compound were given to six normal ewes for periods of four to six weeks before lambing in the hope that it might provide a clue to a type of substance capable of depleting tissue copper. This had no effect on the copper status of the mothers and all lambs were born normal. Concomitant copper balance studies by Burdin (unpublished) at Weybridge, on sheep in metabolism cages, showed that daily injections of B.A.L. did not in fact deplete tissue copper when continued over a period of 4 weeks; blood copper values remained normal and liver tissue showed no diminution in copper content. A slightly increased urinary elimination of copper occurred over the first few days but this was quite transitory and did not affect the monthly balance sheet.

Our present view is that the unknown factor is one affecting the copper storage function of the liver, but that it is not molyb-

denum.

The "enzootic jaundice" of sheep in some parts of Australia, where an unknown factor seems to operate in the reverse way, causing enormous retention of copper in the liver and symptoms of copper poisoning on pastures quite normal in copper content, has not been observed in Britain. In the observations of Bull (1949) a high normal copper content in plants (15 p.p.m. or

more) associated with a very low molybdenum content (0.1 p.p.m. or less), giving a very high Cu/Mo ratio, favoured the development of an excessively high copper status in sheep. The extraordinarily low pasture molybdenum figures given by Bull, down to 0.03 p.p.m., have not yet been encountered in Britain.

True copper poisoning is, of course, well known in sheep grazing in English orchards sprayed with cupric insecticides, and in this connection it is interesting to note that symptoms do not develop for many weeks and may even appear several weeks after removal from the contaminated vegetation. Apparently the liver becomes packed with copper and break-down of function then occurs quite suddenly.

Apart from "swayback" other clinical manifestations of "copper deficiency," either direct or "conditioned," have not been reported in sheep in Britain, although experiments are now in progress on ewes displaying low copper status in areas in which swayback is not prevalent. It is believed that absence of symptoms in apparently normal hypocupraemic ewes may be deceptive and that in some cases elevation of copper status would be beneficial.

#### Cattle

It was not until 1946 that the occurrence of hypocupraemic disorders was established (Allcroft 1946 and Allcroft & Parker 1949) in cattle in Great Britain although such disorders had

then been known in sheep for eight years.

The two dairy farms on which it was first observed are near the Shropshire-Cheshire border and are situated entirely on flat peat land just below sea-level. The chief clinical features of the disorder were chronic diarrhoea and unthriftiness especially during the grazing season. Because of the almost constant scouring the cows were in poor condition, with rough staring coats, and gave low milk yields, but it was in young stock between weaning and calving that unthriftiness was most marked. These animals were severely stunted, so much so that 2-year old heifers could be mistaken for 8-10 month old calves. These symptoms suggested analogy with "peat scours" of New Zealand described by Cunningham (1944).

Blood samples from both herds showed that copper values were very low, figures of 0.01 to 0.04 mg./100 ml. with a mean of 0.03 mg./100 ml. being found. The liver copper value of one cow which had been on the farm for 6 years was as low as 5.7 p.p.m. on a dry matter basis, with a corresponding blood copper

value of 0.06 mg./100 ml.

Pasture samples taken from fields on both farms at intervals throughout the year gave normal copper values ranging from 8 to 23 p.p.m. on a dry matter basis with a mean of 14 p.p.m. Molybdenum values ranged from 2.3 to 7.4 p.p.m. with a mean of 4.4 p.p.m. Although these are slightly higher than the usual

normal of 0.5 to 2 p.p.m. found in Great Britain they do not approach the "teart" pasture values of 15 to 80 p.p.m. found in Somerset by Ferguson, Lewis and Watson (1943).

Daily administration of 2g. copper sulphate to a group of 8 cows on the larger of the two affected farms resulted in a rapid improvement in clinical condition and milk yield. Blood copper values increased to normal levels of 0.07 to 0.09 mg./100 ml. within two months and were maintained as long as copper therapy was continued. In a similar untreated control group blood-copper levels remained low throughout an experimental period of 18 months, mean monthly values ranging from 0.02 to 0.05 mg./100 ml. Limited haematological studies indicated that there was no anaemia associated with the hypocupraemia. All the calves on this farm showed normal blood copper values for the first 9 months of their lives, probably because they were separated from their mothers and fed indoors on calf meal during this period, but there was a steady decline to average values of 0.04 mg./100 ml. during the next 8 months, associated with grazing for longer periods on the peat pastures.

Transference of two cachectic hypocupraemic 2-year old heifers and a stunted 6 month old calf still with normal blood copper from the experimental farm in Shropshire to normal pasture at the Weybridge laboratory resulted in a marked improvement in clinical condition but not in increased blood-copper values. With the heifers, low values persisted for 15 months; with the calf there was an unexpected decrease to less than one-third normal. Change from grazing to winter feeding in stalls resulted in a rapid increase in blood copper in all three animals. Explanation of the anomalous behaviour of these animals is not apparent yet, although it may be related to the original disturbance of liver functions, but the influence of indoor and outdoor conditions is under specific investigation.

Since these initial observations on "conditioned" copper deficiency in dairy cows in Shropshire, "hypocupraemic" disorders of cattle have been observed in various parts of the country and their incidence and distribution are at present under investigation. Because of the possible economic importance of a subnormal copper status a blood survey of selected herds throughout England, Wales and Scotland is being carried out by the Biochemical Department of the Veterinary Laboratory at Weybridge in collaboration with local Veterinary Investigation Officers, in the hope that hypocupraemia will point the way to closer clinical observations and treatment of subnormal con-

ditions.

During the last 15 months 125 herds in England and Wales have been investigated and of these one third showed hypocupraemia associated with a variety of clinical conditions, many of them readily responsive to copper therapy. The general distribution of observed affected herds is indicated roughly on the provisional map shown in Fig. 2, but it is believed that extension



Figure 2.—The black dots on the map of Great Britain indicate areas where hypocupraemic disorders of bovines have been observed during a "blood copper survey" of selected herds during the last 11 months.

of the survey will demonstrate a much more uniform geographical scatter.

Certain areas in Scotland have been subjected to more intensive investigation and in the county of Caithness over 200 farms have been surveyed because of the occurrence there of a copper deficiency syndrome which so far appears to differ from those observed in other parts of Britain. Of the 200 herds investigated 70 percent were found to be hypocupraemic. In Caithness where cattle are chiefly of the beef breed, it is the calves which are affected much more than the cows. Details of this condition have been described by Jamieson and Allcroft (1950) under the name "Copper Pine." The disorder occurs mainly in cross-bred Aberdeen-Angus and in cross-bred Highland calves. In this country cattle are housed in the winter, calves are born during April and May and are then pastured with their mothers until the calves are sold in autumn at about 6 months old.

The first symptoms usually appear about a month after turning out to grass. The calves show a stilted gait, progressive signs of malnutrition follow, and the coat becomes rough, dull and discoloured. In some cases there is a definite change of colour of the black hair around the eyes to grev so that calves have a definite "spectacled" appearance. Diarrhoea is not a constant feature and anaemia is not evident. Unthriftings becomes more marked as the animals continue on pasture and after about four months the appearance is similar to that shown in Fig. 3. In some seasons the condition develops more rapidly than in others and death may occur at about 4 to 5 months of age. Affected animals which survive and are retained in the herd improve under winter conditions of management, but can be recognized easily the following year by their subnormal development. The typical clinical condition, however, does not recur when they are on pasture during their second year and general appearance improves in later years. The incidence of clinical cases is usually in the region of 25 per cent of the calf population grazing affected areas, but varies on different pastures. In some instances practically all the calves become obviously affected.

Four farms were selected for preliminary experimental observations because of their high incidence of pining in calves. Blood copper values for both cows and calves on all four farms were low, averaging 0.03 mg./100 ml. Pasture samples showed copper figures ranging from 4.8 to 20.8 p.p.m. on a dry matter basis. Apart from the one low figure of 4.8 p.p.m. on a sample of herbage from very rough grazing all the other values fell within the usual normal range of 7 to 24 p.p.m. reported by Eden (1944) for parts of England and Wales. Molybdenum values varied from 1.4 to 19.5 p.p.m. on dry matter on samples from different fields on the four farms. It should be pointed out that the quality of pastures on most farms in Caithness is good.

and that there is no question of the pining condition being associated with insufficient calories and protein.

The effect of copper sulphate therapy was observed in animals on two farms in which the incidence of pining was high. On one a small dose was given once only to two groups of three three-month old calves of cross-bred Aberdeen-Angus breed. One group received the equivalent of 50 mg. copper intravenously, the other of 500 mg. of copper by mouth. A similar group of untreated calves served as controls. On the other farm four calves and their mothers were each given 5 grammes of copper sulphate orally (equivalent to 1,250 mg. of copper) at monthly intervals for three months, while a similar untreated group on the same pasture served as controls.

In both experiments blood samples were taken before treatment and subsequently at monthly intervals. At the end of four months, when the calves were 6 to 7 months old, two untreated control calves and one treated calf from each farm were killed for post-morten examination and estimation of copper in selected tissues.

The results showed that when only one small dose of copper was given, either orally or intravenously, copper figures for blood and tissues were not raised to normal levels, but that clinical symptoms of pine were nevertheless prevented and apparently normal development continued. Fig 4 shows a calf of similar age and breed to that in Fig. 3. Both were kept under identical conditions on the same pasture, the only difference being that the calf in Fig. 4 received 50 mg. copper intravenously when 3 months old. The live weight of this calf was 448 lb. as compared with 336 lb. for the untreated calf shown in Fig. 3. In spite of the prevention of symptoms of pine, all blood copper values throughout the experimental period remained low averaging only 0.03 mg./100 ml. Liver copper was almost as low in the treated calf in Fig. 4 as that in the untreated control calf in Fig. 3, the values being 5.5 and 4.2 p.p.m. on dry matter, respectively. In view of the short period of observation, comments on these findings are reserved until the results of current investigations are available.

Where larger supplements of copper were given orally at monthly intervals, blood copper values in both calves and cows increased throughout the experimental period. Mean values for the calves increased from 0.05 to 0.07 mg./100 ml and those for the cows from 0.03 to 0.07 mg./100 ml. Values for untreated controls fell in a similar manner in both groups. The higher copper supplement increased liver copper storage, since a value of 18.9 p.p.m. on a dry matter basis was found in a treated calf, compared with 5.2 p.p.m. in the liver of an untreated control. Even so, a liver value of 18.9 p.p.m. Cu on dry matter is on the low side for a calf of seven to eight months of age. Although the exceedingly small single dose of copper actually prevented pining for the short period concerned, it is probable that doses large enough



Figure 3.—A 6-month old cross-bred Aberdeen-Angus calf showing "copper pine" after grazing on pasture in Carthness for 4 months. Live weight, 336 lbs.



Figure 4.—A calf of the same age and breed as shown in Figure 3 and grazed on the same pasture, but received 50 mg. of copper as copper sulfate intravenously once only at 3 months of age. Live weight, 448 lbs.

to maintain normal values in blood and liver would give better growth and development rates.

It is of interest to note that no anaemia has been observed in this pining condition in calves. Haematological studies made throughout the experimental periods showed that the blood picture was normal in both untreated 'pining' calves and in copper treated healthy calves. In this respect as well as others the condition differs from copper deficiency disorders described by Bennetts et al (1941) in Australia, Cunningham (1946) in New Zealand and Davis et al. (1946) in Florida.

Repetition of these experimental observations the following year gave similar results. Extended biochemical observations showed that there was no difference in ascorbic acid content of livers and adrenals of 'pining' and copper treated calves nor was there any increase in inorganic P values of the blood as observed by Davis & Hannan (1947). No difference in serum albumin and globulin or total serum proteins was observed but preliminary results of electrophoretic analysis of serum indicate a lower B-globulin content in 'pining' calves.

It has been suggested by analogy that this pining condition in calves in Caithness is due to excess molybdenum in the pastures, and it is true that two fields on one farm where the disease occurs showed the relatively high molybdenum contents of 19 and 16 p.p.m. D.M., but it should be emphasized that calves pined equally quickly and severely on other fields on the same farm where molybdenum values were only 2 to 4 p.p.m., and on adjoining farms where molybdenum values were 1 to 5 p.p.m.

Thus the identical clinical syndrome occurs on pastures of widely different molybdenum contents and it does not seem at this stage that there is sufficient evidence to indicate that molybdenum in these Caithness pastures of normal copper content has anything to do with the low copper status of calves and cows. It is believed that some other "conditioning factor" is involved.

To get more information on optimum dosage levels of copper, and to find the most economical way of supplying adequate amounts of this essential trace element to beef cattle under existing methods of husbandry, various treatments have subsequently been tried on several farms (Jamieson & Allcroft 1950).

On some farms mineralized cubes supplying copper at the rate of 0.3 g. per head per day were fed to cows throughout the gestation period. Observations were made on groups of calves from treated and untreated mothers, and in some groups extra

copper was also supplied to the calves.

On other farms no copper supplements were given to the pregnant cows or to the calves but the pastures were top-dressed with copper sulphate during March at the rate of 10 lbs per acre and subsequently grazed by the cows and calves from May until October.

The results of these experiments are not all available yet

but it is evident that pining in calves can be controlled by giving adequate copper supplements to the mothers during the gestation period and by top-dressing the pastures with copper sulphate, although it is doubtful if the latter method would control the disorder unless the pastures were top-dressed anually. Although clinical symptoms of pining were prevented by these two methods of treatment, other results showed that greater gains in weight resulted in calves from treated mothers if extra copper supplements were also given to the calves themselves.

There is still much to be learned about hypocupraemic disorders and methods of treatment and in our present state of limited knowledge caution must be exercised in the interpretation

of data.

#### COPPER-MOLYBDENUM RELATIONSHIPS

McCollum et al (1939) showed that the hair of rats on an experimental diet deficient in copper becomes depigmented. Since depigmentation of hair had been reported in Holland in cattle suffering from scouring diseases attributed to copper deficiency, and change of coat colour (not true depigmentation) is associated with scouring in the "teart" areas of Somerset, and since both disorders could be prevented and cured by administration of copper sulphate, Russell (1944) suggested that this might be taken as presumptive evidence of copper deficiency in "teart" cattle. She predicated abnormal intake of molybdenum as interfering with the utilization of copper, and reviewed the literature on "teart" in the light of "conditioned copper deficiency." The Australian work of Dick and Bull, (1945) recorded observations indicating that high molybdenum intake in a diet reduced the storage of copper in the livers of cattle and sheep, and brought copper-molybdenum relationships into prominence, and Cunningham in New Zealand (1946) suggested that "peat scours" may be the result of a small excess of molybdenum in the pastures superimposed on a moderate deficiency of copper. Later Cunningham (1949) confirmed the observations of Dick and Bull and showed that a high intake of molybdenum over a prolonged period did reduce liver copper storage; also that it reduced blood copper levels in bovines. This effect of molybdenum on copper storage was confirmed later in the same year by Comar et al (1949). Recent results obtained at Weybridge on the effects of prolonged high molybdenum intake on bovines whose copper status was normal before molybdenum administration was commenced, are in line with these observations and reduced liver copper storage has been found but they differ from Cunningham's observations (1949) in that there has been no concomitant decrease in blood copper levels over experimental periods of six to eighteen months. Liver copper values obtained from biopsy samples showed a considerable diminution, while blood copper remained practically constant. It is of interest, however,

that when similar amounts of molybdenum were given to young bovines of initial low copper status brought in from Caithness (liver values 6 to 11 p.p.m.) instead of a reduction there was an increase in liver copper storage associated with an increase in blood copper levels. This latter experiment has been running for only six months and it is too early to say what the final effect will be but these preliminary observations are in line with those obtained at Weybridge in 1948 on sheep of low copper status brought in from Derbyshire. In this experiment six hypocupraemic ewes were transferred from a "swayback" farm to stalls at the laboratory. Two were retained as controls and sodium molybdate administered to four over a period of 15 months in daily doses raised each quarter on the scale 14, 56, 112, 224 mg. Mo. In the later stages blood molybdenum values were running at 100 times normal. Despite this, blood copper levels rose rapidly, from the low average of 0.025 mg./100 ml. to a normal of 0.085 mg. during the first quarter, continued to rise and remained about 0.10 to 0.12 mg./100 ml. in the later stages. This is illustrated in the graph of Fig. 5. At the conclusion of the experiment liver tissue had reached a mean value of 528 p.p.m. on dry matter, as compared with 512 p.p.m. for one of the control sheep and a calculated initial value of about 15 p.p.m. (found in similar sheep on the same "swayback" farm). All six sheep improved in weight on the liberal stall ration, which had an estimated copper content of about 8 p.p.m. on dry matter, and remained in excellent condition throughout with no sign of scouring. In this experiment high intake of molybdenum not only failed to maintain the initial low copper status of the sheep but permitted rise of both blood and liver values to normal levels.

It is difficult at this stage to offer an adequate explanation for the conflicting effect of a high molybdenum intake associated with normal dietary copper, on liver copper storage in animals of initial normal and of initial low copper status but for the moment two factors may be predicated, (a) molybdenum, which may function as a normal regulating factor in liver copper storage and (b) another even more powerful unknown factor which is the operative one in the Derbyshire "swayback" area, where molybdenum content of pastures is normal, and in the Caithness area where "copper pine of calves" is apparently independent of molybdenum intake. In (b) the primary cause of low copper status is not molybdenum and hence mere removal of that cause permits the copper status to return towards normal despite molybdenum subsequently superimposed.

Since no observations on the copper status of animals in the "teart" area of Somerset were reported by Ferguson, Lewis and Watson (1943) a series of investigations was undertaken by the Biochemistry Department at Weybridge in 1947. Blood samples were obtained from cattle which had not had prophylactic copper supplements ("anti-teart" cake) on "teart" farms were generally found to show low blood copper but "hypocupraemic

scours" was also prevalent outside the actual "teart" area, and even within it some farms were found with high pasture molybdenum but with blood copper values above those on adjacent low molybdenum pastures. No clear relationship between blood copper and blood molybdenum could be discerned. Pasture copper on all farms investigated was normal or even high.

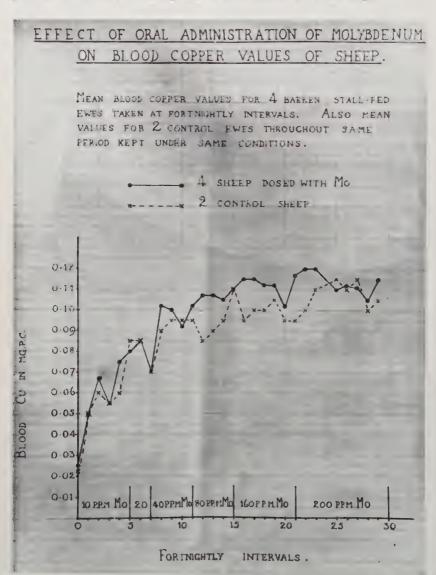


Figure 5.—Graph illustrating increase in blood copper levels of hypocupraemic sheep on a high molybdenum intake over a period of 15 months.

Six normal heifers sent from Weybridge to a "teart" farm in Somerset, of pasture molybdenum ranging from 16 to 40 p.p.m., commenced scouring in one to two weeks and were left to scour continuously for a further four weeks, during which time no consistent change in blood copper occurred, despite elevation of blood molybdenum. At this point three of them were intravenously injected once only with 300 mg. Cu. as sulphate. Scouring was immediately arrested and did not return for four weeks. In the fourth the scouring was controlled for a similar period by the usual daily oral administration of 2 g. copper sulphate. The remaining two served as controls and continued scouring for six weeks until the pasture became "non-teart" after frosts. Appreciable fall in blood copper ensued in these two, but it is believed that this could have happened with equal probability on a similar Somerset pasture of the non-molybdeniferous type on which "hypocupraemic scours" occurs. Observations on these six heifers has been continued over a further two "teart" seasons (spring and autumn). Scouring in four of them was again controlled by intravenous injection of 300 mg. Cu as sulphate. During the 18 months that these animals have been on the farm four of them have had 300 mg. Cu intravenously on three occasions at approximately 6 monthly intervals. The two controls have been left untreated. There is now a marked difference in the clinical condition between treated and untreated animals. The controls show the usual unthrifty appearance of "teart" animals and their blood copper values have remained between 0.03 and 0.05 mg./100 ml. for about 12 months. Blood copper values of the injected animals averaged 0.075 mg./100 ml. over the same period and their clinical condition was much better than the two controls although insufficient copper had been given to maintain them in first-class condition.

As for sheep, blood copper levels in a flock of 40 ewes brought in from another area on to the same "teart" farm did not show similar diminution of copper over the same period. Average blood copper figures were still normal at 0.095 mg./100 ml., after they had been on the farm for three months, although molybdenum values were elevated to 0.082 mg./100 as compared with a common normal of 0.005 mg. Six months later average copper and molybdenum values were 0.089 and 0.098 mg./100 ml. respectively and a year later copper figures had not fallen below 0.075 mg./100 ml. in spite of elevated blood molybdenum. Twenty sheep which had been on another farm with pastures of high molybdenum content for three years showed mean blood copper and molybdenum levels of 0.07 and 0.06 mg./100 ml. respectively. No cases of swayback have been observed on any "teart" farms at all, so far as can be ascertained, and certainly none have occurred during the last three years when farms running sheep have been under our own observation.

The contrast between occurrence of "swayback," with very low blood copper levels, on the Derbyshire pastures of low molyb-

denum content, and the non-occurrence of the disease associated with much higher copper levels on the Somerset pastures of high molybdenum content, is very striking. Obviously the factor inducing low copper status in ewes and demyelination in lambs in Britain is distinct from molybdenum and operates more quickly. High molybdenum *per se* in pastures not only fails to induce "swayback" but fails to induce hypocupraemia in sheep to anything like the extent it does in cattle.

Experiments on stalled cattle at Weybridge in 1948 showed that daily administration of a few grams (2.3 to 6.9) of sodium molybdate produced scouring even on winter rations in 16 to 24 days but some animals were more resistant and did not scour even after six weeks although there was marked loss of condition. Depression of blood copper did not occur and in each of the eight experimental animals there was an increase over this period, from a mean of 0.07 mg./100 ml. to a mean of 0.104 mg./100 ml. despite enormous elevation of blood molybdenum (40 to 200 times). Heifers placed on Weybridge pasture with a copper content of 11 p.p.m. D.M. dressed with molybdate to elevate it to 40 to 60 p.p.m. Mo D.M., scoured severely in five days without significant change of blood copper level but with greatly raised molybdenum level. Injection of 500 mg. Mo as sodium molybdate intravenously on three successive days failed to produce scouring or alteration of blood copper in two cows. No liver biopsy samples were taken during these observations to check its effect on liver copper storage, but recent experiments on three heifers placed on the molybdenised Weybridge pasture indicate that there was an appreciable fall in liver copper values with onset of scouring in 11 days, although there was no fall in blood copper. These preliminary observations require confirmation and, doubtless, some ingenuity in interpretation.

The scouring induced by molybdate administration in stalls or on molybdenised Weybridge pasture could be controlled by oral administration of copper at the usual daily rate, either as the sulphate, carbonate or acetate, but it was observed that single intravenous injections of smaller amounts were more effective. As little as 100 mg. Cu controlled scouring in young animals for several weeks despite continued ingestion of molybdate. This effect of intravenous copper therapy does not support the theory for copper-molybdenum action suggested by McGowan, Brian and Blaschko (1947) without confirmation by experimental work, but is in line with the observations of Davis and Kidder (1949) to the effect that symptoms of molybdenosis are probably not caused simply by uncontrolled bacterial activity in the gastro-intestinal tract.

Nevertheless the "scouring" of "molybdenosis" seems primarily due to disturbance within the alimentary tract, and not to molybdenum circulating in the blood stream. The function of copper, administered *per os* or intravenously, in controlling diarrhoea as such, is under further investigation. Diarrhoea

occasioned by some forms of bacterial infection can be similarly controlled.

#### FLUORINE

Although fluorine occurs in appreciable quantities in bones and teeth it is not regarded as an essential micro-nutrient and until recently it was considered entirely harmful and only unavoidablely present in animal tissues. Traces are now regarded as useful in protecting against dental caries and, for human beings, water supplies containing up to 0.5 p.p.m. are regarded as beneficial although levels exceeding 2 p.p.m. are definitely harmful. Its significance in animal health only arises when larger amounts are ingested, and this usually occurs by contamination rather than by the presence of abnormally large amounts of fluorine in vegetation, the content of which remains low even when growing on soils very high in the element. The "Oxford Clay" soils containing about 400 p.p.m. of fluorine only show pasture values of 4 to 7 p.p.m.

Spontaneous fluorosis is found in many parts of the world, the most notable diseases being the "darmous" of the rock phosphate areas of Morocco and Tunis and the "gaddur" of the volcanic soils in Iceland. It is the natural water supply which is generally at fault. Darmous is particularly common in sheep, which may die of malnutrition caused by wearing down of the incisors and dystrophy of all the permanent teeth.

The use of ground rock phosphate as mineral supplement for cows has occasioned severe fluorine cachexia accompanied by reduced milk yield, lameness, exostoses on long bones and mandibles, hypoplasia of dental enamel, and other changes. Use as

fertilizer is of course quite safe.

The most serious outbreaks of fluorosis in Britain have been of industrial origin, and caused by surface contamination of pastures in the direction of the prevailing winds from large factories emitting fluorine compounds. Since the extent of "industrial fluorosis" in grazing animals is now known to be far greater than formerly believed, it may be of interest to mention a few outbreaks which have been investigated over the last 12 years by the Weybridge laboratory in co-operation with local veterinarians. The data up to the year 1946 have been published by Blakemore, Bosworth and Green (1948) but a brief recapitulation may be presented here.

Shortly before the war serious lameness of dairy cows came under investigation in the vicinity of large brick factories in Bedfordshire, and clinical examination by the local veterinary investigator suggested the fluorosis described in Italy in 1912 in association with a superphosphate factory. This diagnosis was quickly confirmed by pathological and biochemical examination of bones of affected animals. Enormous values for fluorine were found, 1.0 to 2.7 per cent expressed on the "bone ash," as

compared with 0.05 to 0.08 percent for normal cattle in other areas. During life affected animals excreted up to 68 p.p.m. in the urine as compared with less than 5 p.p.m. for normal cattle or less than 10 p.p.m. for cattle several miles away from the nearest factory chimneys. Analysis of samples of urine, as well as of pasture grass and hay, served to construct a map of the affected area. This was found to stretch for about 5 miles along a chain of factories, clinical cases being most severe within a mile of each set of chimneys. Where pasture contamination exceeded 25 p.p.m. on the dry matter severe skeletal changes occurred, provided exposure to risk was long enough. At lower levels of contamination, about 14 p.p.m., milder cases occurred, evidenced by mottling of the teeth.

The origin of the fluorine was found to be the self-burning clay used for brick making, which contained 500 p.p.m. of fluorine and 10 per cent of organic matter. It is the presence of this organic matter which makes the clay so valuable, renders the bricks self-burning, economises in fuel, and improves the texture of the bricks by ensuring even incineration. Each large chimney serves a series of brick chambers at various temperatures, the gases from the hotter chambers serving to dry the wet bricks in the cooler chambers and finally bring them to ignition point, after which they finish at a bright red heat of their own accord. At intermediate temperatures a small amount of oil is formed by destructive distillation and at the highest temperatures silicon flouride is given off. The mixed effluents react in the chimney to form an aqueous oily mist together with gaseous products. Both contain fluorine compounds but only the oily mist particles are heavy enough to be carried down on to the pastures within a mile of the chimneys. These settle on the grass, or are caught by hay, as a dusty oily film, and account for the ingestion of fluorine by the cattle. Hay close to the factories may reach a fluorine level of 100 p.p.m. The contamination is entirely on the surface of the grass. Any fluorine compounds washed into the soil by rain are fixed there in insoluble form and do not enter by the plant roots. Hence the leaves of "root crops" are high in fluorine while the fleshy parts are normal.

Enquiry showed that mild fluorosis must have existed in the area for many years but remained undiagnosed until the expansion of the local brick industry reached a point at which gross contamination of the pasture caused skeletal exostoses and actual lameness in the grazing dairy cows on neighboring farms.

Soon after this, fluorosis in cattle and sheep was investigated in Scotland in connection with the large aluminum factories at Fort William. In this case the origin of the fluorine was the cryolite used as flux in the electrolytic process. Because of the peculiar drift of slow winds in hilly country, contamination of pastures was observed for several miles from the factories, although severity of lesions in animals was not so great as in Bedforshire. The factories are now under reconstruction, with re-

placement of old furnaces by more modern types fitted with

"scrubbers" to prevent atmospheric pollution.

About 1945 a third type of industrial fluorosis came under observation in England in the vicinity of open-air calcining of iron-stone.

The local process consists in mixing the damp iron-stone with about 7 per cent of coal, and heaping the mixture into ridges running round the section from which the ore is being lifted. The ridge is then ignited, further layers of coal and ore being added until a height of about 40 feet is reached. The calcining takes about six weeks to complete and the whole discharge of smoke is concentrated at one point in the direction of the prevailing winds for a relatively short time, but during this period contamination of adjoining pasture may be very high and persist indefinitely in harvested hay crops. The exterior of a hay-stack half a mile from a burning ridge showed 490 p.p.m. of fluorine in the exterior layer and 70 p.p.m. at a depth of 2 feet. The object of the calcining is to reduce the weight of the ore and transport costs, and to render it physically suitable for the blast furnaces at smelting centres. The fluorine content of the fresh ore is about 0.12 per cent and of the calcined ore about 0.03 percent, so that three-quarters of the fluorine compounds pass off in the smoke, the particles of which serve as "vehicle" carrying the contamination on to pastures for a distance of about a mile in the direction of the wind.

Yet another outbreak of fluorosis in cattle was encountered in the neighborhood of a colour and enamel factory, and at the present moment several outbreaks are being investigated, both in England and Scotland, in the vicinity of large steel works which use sodium fluoride as flux in the "open hearth" process.

The problem of control of industrial fluorosis can be solved in two ways, one by fitting appliances for trapping the gases and preventing atmospheric pollution; the other by conducting agricultural operations with the known "fluorine hazard" in view e.g. by cultivation of root crops and limiting use of pasturage to short periods of time. Store cattle can usually be fattened on contaminated pasture for a few months but dairy cattle cannot be maintained on affected farms all the year round.

The sequence of events with fresh animals brought on to badly contaminated pasture or hay may be sketched as follows: (1) fluorine is absorbed into the blood stream in amounts depending on the degree of contamination (2) most of this is eliminated in the urine, quickly leading to high "ingestion values," quite commonly 25-70 p.p.m., (3) portion of the circulating fluorine is slowly fixed in the bones, which in the course of six to twelve months may reach values sufficiently high to be reflected as skeletal exostoses and clinical lameness (circa 10,000 p.p.m. on the "bone ash," Fig. 6 shows typical exostoses on the hind limb of a cow), (4) on removal from the source of contamination and feeding on normal rations the urine values rapid-



Figure 6.—Bones of the lower limb of a cow showing extensive exostoses. Fluorine content of the exostoses was 13,000 p.p.m. on the bone ash.

ly fall, but remain considerably above normal (circa 12-15 p.p.m.) for a very long time because of slow removal of stored fluorine from the skeleton in the ordinary course of slow reconstruction of fresh bone; urine values at any given moment are a balance between "current ingestion level" and "skeletal change value"; the urine figures at pasture tend to reflect the current fluorine level of ingested food; a week after transfer to normal rations urine values tend to reflect storage levels and hence the degree of fluorosis, (5) adult animals show no symptoms for many months, and if the contamination is small may not show symptoms for several years, (6) young animals reflect ingestion of small amounts of fluorine by "mottling" of the growing teeth, and degree of contamination of pastures may be such that only young animals reveal it in clinically recognisable forms; the first signs of "clinical fluorosis" should be looked for in the growing teeth of young animals or in slight lameness and cachexia of adult animals.

The easiest method of diagnosis of "incipient fluorosis" is by analysis of the urine of suspected clinical cases, or of apparently healthy grazing animals in suspected districts. Any value below 5 p.p.m. is normal. Any value above 10 p.p.m. in urine is suspicious, and when values exceed 20 p.p.m. a survey of the district for source of industrial contamination is imperative, since legal claims by farmers for compensation may assume

serious proportions.

A word of warning should be inserted, however, regarding interpretation of analytical data in relation to legal claims, which are only legitimate in relation to actual economic loss. Urine values reflecting current ingestion may be temporarily high without serious clinical effects. Pasture values are often erratic and short grass behind long grass may be protected. Clinical examination, particularly for dental changes in calves and lameness in cows, is the best guide to severity of fluorosis. It is only when teeth are so badly affected as to interfere with mastication, and skeletal changes so advanced as to cause discomfort, that milk vield is seriously interfered with.

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## TRACE MINERALS IN NEW ZEALAND

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The agricultural industry of New Zealand has developed chiefly around the production from animals of commodities which can be exported and sold on overseas markets. Such a development has been encouraged by a favourable climate with no great extremes of temperature and with a well distributed rainfall, while a small population and restricted availability of labour have dictated that the highest return must accrue from minimal labour output. The system of farming evolved to meet these circumstances is one in which grazing animals convert permanent pastures, and occasionally other crops, into meat, wool and milk or milk products. The almost entire dependence on pasture for stock food means that each farm is self supporting for its fodder supply, and the high productivity of the land and high carrying capacity has led to the farm unit being relatively small. In consequence New Zealand's stock population can be regarded as made up of many groups of animals, each dependent for its nutrition on food produced within the limits of a small area.

Such conditions offer the maximum opportunity for the development of deficiency disease symptoms in farm animals, should the soils be lacking in any of the essential mineral elements. In certain areas cobalt, copper or iodine has been found deficient to a degree that stock disease results; in some areas there is a dual deficiency of copper and cobalt; and in others there is a copper deficiency accompanied by an excess of molybdenum, which aggravates the deficiency of copper in animals and causes additional disease symptoms. In yet other areas sheep are susceptible to a disease the symptoms of which resemble copper poisoning, though excess copper does not occur in the fodder or soil. A low content of fluorine in New Zealand river waters has been observed and, though no symptoms in animals have been associated with this, the possible significance as a cause of dental caries in humans is under study.

Trace mineral deficiencies different from those known to affect animals have been observed in the plant world. Molybdenum deficiency occurs in cauliflowers and in clovers, and boron deficiency affects both fruit trees and turnips. The possible influence that cultural and fertilizing practice may have in hastening or inducing a trace element deficiency in threshold soils has been noted by the effects and lesions produced in some crop plants. This is referred to in connection with boron deficiency where the heavy use of lime may be a precipitating factor.

Details of the deficiencies mentioned above are discussed be-

low in separate sections.

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#### COBALT DEFICIENCY.

Cobalt deficiency disease in New Zealand has been known as "bush sickness," "Mairoa dopiness" and "Morton Mains disease," all of which were local names applied to a progressive anaemia and wasting which occurred in cattle and sheep grazed in the deficient area. Bush sickness was first called "bush disease" by Park (1) in 1897 because it was thought that the disease was a legacy from the heavy bush that had covered the land before it was developed into pasture land; the name was changed to "bush sickness' by Reakes in 1912 (2) in an attempt to avoid this misconception since by that time it was realised that the disease could occur on soils which had never carried bush. The term bush sickness is now used as a local popular name for cobalt deficiency disease in cattle and sheep in the Nelson district of the South Island and in the North Island except for the Majora district. "Maiora dopiness" refers to a similar wasting disease of sheep in the Majora district of the North Island though in this case as an additional symptom of the disease the bones have been described as light and very fragile (3), (4). "Morton Mains disease" is the local name for a rather less severe deficiency of cobalt which affects chiefly young lambs in parts of the Southland district of the South Island (5).

Investigation into bush sickness in New Zealand commenced about the turn of the present century and attention was fo-



Figure 1.—Cobalt deficient hill land in New Zealand receiving treatment with this element by dusting from the air.

cussed on the most prominent symptom, a progressive anaemia. This suggested to Park in 1898 (6), and to Aston in 1912 (7) that the provision of iron might be beneficial to the stock. Aston developed the iron deficiency hypothesis over a number of years (8), finding less iron in sick pastures than in healthy pastures and eventually effecting cure and prevention of bush sickness by feeding iron compounds, the most successful of which was limonite mined in New Zealand (9). Though there was a large measure of success following the generalized use of limonite there were, nevertheless, some disappointments since not all limonites were equally effective and some proved useless (10). An adequate explanation of the variation in the efficiency of limonites due to variation in their cobalt content was forthcoming after the Australian workers Filmer and Underwood (11) had shown that a cobalt impurity in the limonite was the effective fraction in curing a similar disease named Enzootic Marasmus and affecting cattle and sheep in Western Australia. The application of the results of Australian work to New Zealand showed that the three diseases referred to above all yielded to treatment by cobalt. The development of sensitive chemical methods in New Zealand enabled it to be shown that in cobalt deficiency areas the soil (12), (13), the pasture (14) and the animal (15) all contain less cobalt than similar samples from healthy areas. Mc-Naught (15) has worked out the limits of the contents of cobalt in pastures and in animal livers which are indicative of cobalt



Figure 2.—"Bushsickness" in a young cow induced by cobalt deficiency in the soil and the forage growing on it prior to treatment.

deficiency, and this basis is now regularly employed as a diagnostic procedure for cases of suspected cobalt deficiency. For sheep three months and older, concentrations of below 0.06 parts per million cobalt in the liver indicate deficiency and above 0.1 parts per million, sufficiency; for yearling and mature cattle the level indicating deficiency is 0.05 parts per million and for sufficiency, 0.12 parts per million or higher. Pastures which contain less than 0.07 parts per million cobalt are regarded as deficient.

Affected soils.

The affected soils of the North Island are coarse pumice types derived from the Taupo and Kaharoa ash showers and heavily leached parts of the Mairoa ash shower. This information permits of mapping in broad terms the distribution of possible cobalt deficiency areas in the central part of the North Island, and this system of mapping on soil type agrees well with the occurrence of clinical symptoms in the animal population.

In the South Island and Nelson soils are for the most part of granitic origin and the Morton Mains soils are derived from

glacial rock-flour or loess.

The most significant feature of the cobalt deficient soils is

their coarse structure and ready leaching character.

Another feature is the capacity of many of the cobalt deficient soils, when suitably fertilized with superphosphate, to grow quantities of pasture of good quality apart from the low content of cobalt. The low cobalt content in soil has no limiting

effect on pasture production.

The value to be derived from modern methods of soil classification in the delineation of possible areas of deficiency has been demonstrated by Taylor (16) and Grange and Taylor (17). Taylor's (18) most recent work classifies soils on a genetic basis which shows the inter-relationships of the various soil types. The latter are grouped in suites derived from various parent materials, and within the suite they are arranged in sequence expressing increasing stages of leaching, podzolization. gleying, or other soil process. By a study of the parent material and of its descendents it is possible to determine whether the soil is inherently deficient in any mineral and, if it is not, whether and at what stage of processing a deficiency shows up. An inherited deficiency is found in the intrazonal soil group known as Yellow Brown Pumice Loams where the parent material is a rhyolytic pumice very low in cobalt bearing minerals. In other cases, cobalt deficiency occurs only in the more leached types in certain soil suites, where the loss by leaching is in excess of the replenishment from weathering of soil minerals.

Control.

The control of cobalt deficiency disease in New Zealand has been successfully achieved by the provision of cobalt direct to the animal and more generally by the practice of topdressing the pasture annually, at a rate of 5 oz. per acre, with cobalt sulphate, usually mixed commercially with superphosphate to form cobaltized superphosphate (19).

Though the modern concept of cobalt action is turning from a direct effect of cobalt to the belief that its effect is indirect and possibly obtained through its action on ruminant microorganisms, it is nevertheless still true that the practical method of controlling cobalt deficiency disease is to provide cobalt to the stock.

This has presented problems to New Zealand farming industry since some of the deficient country is not accessible to farm machinery and some is even too rugged and costs are too high for annual topdressing by hand. Attention has therefore been paid to the length of time over which a single topdressing may remain effective. While 5 oz. cobalt sulphate per acre will keep stock healthy if applied each year it has been found that 20 oz. per acre has maintained pasture levels of cobalt and the health of grazing stock at a normal level for a period of at least 7 years (20). This work was carried out on flat country and now is being repeated on steep country (21) on which the washing action of rain on the cobalt may be different. The results obtained up to the present time show that on very steep and hilly country which was topdressed 2½ years ago with 20 oz. per acre the effect of the single topdressing still persists and the pasture is normal in cobalt content. Obviously the acquisition of further information on this aspect is of the utmost importance for land on which the topdressing costs are high.

Technique of distribution over rough country has also been under examination and it has been shown that the use of aircraft is economic and feasible (22). Spreading cobalt on hill pastures through the faeces of sheep drenched with high levels of cobalt is, however, not practicable, since sheep will not tolerate a sufficiently high dose of cobalt to make this method feasible

(23).

A problem of some significance in parts of New Zealand is the effect of a near deficiency or borderline case of cobalt deficiency. Not infrequently the chemical examination of specimens from animals showing some symptoms of unthriftiness gives inconclusive results; the cobalt content is neither low nor normal but is between the two. Further, it is claimed by some farmers on areas on which the classical symptoms of cobalt deficiency do not occur that the provision of cobalt nevertheless results in better growth and higher weaning weights of fat lambs. If cobalt acts, as recent work suggests (24), (25), (26), (27), through growth of ruminant micro-organisms which in turn elaborate a growth factor for the ruminant, then it is not impossible on theoretical grounds that such a borderline deficiency may exist. A partial deficiency of the growth factor would be analagous to subclinical deficiencies of some of the



Figure 3.—Cobalt deficient hill land that has been treated and now carries quite a heavy concentration of stock through the normal grazing season.

growth promoting vitamins. Some work in this connection is at

present being carried out.

The diagnosis of cobalt deficiency disease might at first appear simple; it involves the collection of livers or pasture samples, the chemical analysis for cobalt and the interpretation of the results. However, no one of these three operations is without its difficulties. Pasture samples must not be contaminated with soil otherwise results may be misleading; and livers from new born animals, which are more readily available than adult livers, are not reliable as an index of cobalt status. If some other tissue such as blood, which could be obtained readily and without slaughter of the adult animal, could be relied upon for accurate diagnosis, then the problem of collecting suitable samples would be greatly simplified. The examination need not necessarily be for cobalt; it might be for some product of cobalt metabolism. The chemical methods at present in use for cobalt are accurate and a great credit to their authors; the methods are nevertheless complex and time-consuming to the point that a real practical problem is presented in carrying out any work involving large numbers of cobalt analyses. A rapid. simple and accurate chemical method for cobalt determination is urgently needed. Interpretation presents no problem when cobalt contents found for livers or pastures are very low or are normal, and no cases have been experienced in which a low liver cobalt means anything but cobalt deficiency in the diet; the borderline intermediate value which presents the difficult has been mentioned above.

## COPPER DEFICIENCY.

The existence of a deficiency of copper in New Zealand was first recognized, comparatively recently (28), as one cause of a disease in cattle kept on land reclaimed from peat swamps. It is now known that practically all of the 400,000 acres of peat deposits in New Zealand are copper deficient and that on most of the 250,000 acres of such land developed and used for farming, copper supplements must be supplied to keep stock healthy. The peat soils occur in areas which vary in size from many thousands to a few hundred acres; the larger areas are located in the central part of the North Island and smaller areas at irregular points from the far north of the North Island to the extreme south of the South Island. Most of the deficient peat soils are highly organic, some are mixtures of peat and sand, and others are mixtures of peat and pumice. In some of the peat-pumice mixtures a dual deficiency of copper and cobalt has been found to exist.

Copper deficiency occurs also in leached consolidated coastal sands, on leached sandy soils such as the sandy gum lands, and on other porous soils. The area of copper deficient soils of this nature so far mapped is about half a million acres. The total



Figure 4.—General view of copper-deficient, peat land in New Zealand.

area affected by copper deficiency in New Zealand therefore approaches three-quarters of a million acres. The degree of deficiency of copper, judged by the copper content of the herbage, is not the same in different areas. Two levels of deficiency have been found; one a moderate deficiency, the other more severe. Most of the peat soils produce moderately deficient pastures which contain about 7 parts per million of copper. On the other hand, small areas of peat and most of the leached soils grow more severely deficient pastures which contain about 3 parts per million copper. These values should be compared with the mean for normal pastures in New Zealand, which is 11 p.p.m. of copper.

## Disease in Animals.

In so far as animal disease is concerned, copper deficiency is not the full story. The moderately deficient pastures have, beside their deficiency of copper, a small excess of molybdenum which interferes with the metabolism of copper by grazing animals and aggravates the symptoms of disease in cattle. Such areas are regarded as Complicated Copper Deficiency Areas. On present evidence the more severely deficient areas have no such complication and are regarded as Simple Copper Deficiency Areas.

Cattle and sheep kept on deficient areas for any considerable length of time become severely depleted in copper and the degree of depletion is similar despite the different copper intake from

pastures of the two types of deficiency.

Two distinguishable diseases of cattle occur, one always on complicated deficiency areas, the other on simple deficiency areas. The symptoms of the *complicated deficiency disease* are poor growth and susceptibility to bone fractures in young animals, and in animals of all ages unthriftiness, anaemia, loss of coat colour and an acute debilitating scouring in the spring season when pastures are lush. Symptoms of the simple deficiency disease are similar except that the characteristic seasonal scouring does not occur. In addition, some young calves develop an ataxia associated with regional demyelination of the nervous system.

There is no differentiation in the reaction of sheep to the two types of copper deficiency. Adult sheep are healthy though depletion of their copper reserves may be very severe. Symptoms of disease first develop only in the very young animals which may be affected by an acute osteoporosis or by a permanent ataxia. Ataxia occurs in lambs of from 3 weeks to 4 months of age whose mothers have been on copper deficient pastures for periods of 2 to 3 years or more; osteoporosis occurs in lambs whose mothers have been exposed to a copper deficiency for

shorter periods.

No disease has been observed in horses on copper deficient areas. This may be due, in part, to the use as supplementary

fodder of chaff and oats imported from other areas.

Pigs are reported to suffer from unthriftiness and ataxia but no work has been carried out on this species.

# Molybdenum and Copper.

So close an association exists between copper and molybdenum in animal metabolism that it is necessary to consider both elements when any disease associated with either one is discussed. Dick and Bull (29) showed that increased molybdenum intake will lower the liver stores of copper in cattle and sheep on a normal diet of copper. This has been confirmed for both species. It has been found also that transmission of copper from the ewe to the foetal lamb is greatly reduced by feeding molybdenum to the ewe. The relative amount of copper and molybdenum in the diet determines the effect of molybdenum. In the sheep, for example, if copper in the diet is relatively high, molybdenum feeding does not retard storage of copper in the liver. Storage of molybdenum in the liver is also influenced by the level of copper in the diet. If sheep or cattle with low copper in the diet are fed molybdenum there is a high storage of molybdenum in the liver, but if the intake of copper is increased much less molybdenum is deposited in that organ. In other words, there is in cattle and sheep a reciprocal antagonism to liver storage between copper and molybdenum.

Concerning the pathological effects of molybdenum on cattle,

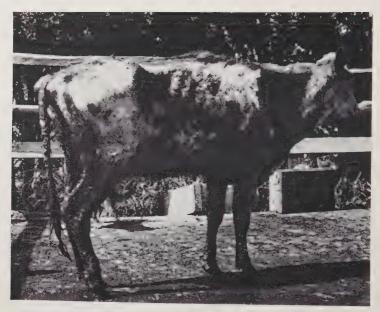




Figure 5.—Copper deficiency in New Zealand cattle, above and below, either induced or augmented by an excess of molybdenum in the forage. Ruminents so affected as these can get little good from their feed, of course, while in such a condition of scouring.

copper has an antagonistic effect also. In peat scours, the copper intake is below normal and a relatively small excess of molybdenum induces pathological scouring, which is readily controlled by small supplements of copper enough to bring the supply to normal. In teart (30), a similar scouring disease, dietary copper is normal and a much larger excess of molybdenum induces pathological effects—control also requires higher copper supplies.

To the occurrence of molybdenum and its effect in animal metabolism are referable some of the features of complicated copper deficiency disease in New Zealand. The content of molybdenum in the pastures varies from summer values of 3 to 7 parts per million to 16 p.p.m. in the spring season, whereas in simple deficiency and normal pastures the content varies from 1 to 3 p.p.m. throughout the year. The excess molybdenum accounts for the fact that the liver copper of cattle and sheep on complicated deficiency areas is lower than would be anticipated from the copper content of the pasture. The greater excess in spring accounts also for the seasonal incidence of scouring in Peat Scours. The inhibition of placental transmission of copper in ewes may be concerned with the occurrence of ataxia in lambs on complicated deficiency areas, but our experience indicates that low copper in the new born lamb does not fully explain the development of symptoms of ataxia.

# Control of copper deficiency.

On simple or complicated copper deficiency areas control is effectively achieved by supplying copper to the stock.

In the case of sheep New Zealand experience has agreed with that in other countries in showing that ataxia in lambs, once developed, cannot be cured but that prevention can readily be achieved by supplying copper to the mother before parturition. For example a weekly dose of 1.5 g. copper sulphate to the ewe throughout the gestation period is effective; so also is the same treatment administered for the last seven weeks before the lamb is born. A more restricted programme of three doses each of 2.5 g. copper sulphate to the ewe at fortnightly intervals about the middle of the gestation period also prevents all symptoms in the lamb but this method is not suitable for general use as 2.5 g. copper sulphate is near a toxic dose for small ewes. It has been found also that ataxia in susceptible lambs does not develop if they are dosed regularly twice each week from birth onwards with 35 mg. copper sulphate in each dose. For cattle, a treatment that temporarily controls the scouring on "complicated" deficiency land is an oral dose of 3.5 g. copper sulphate and this must be repeated each week to maintain control. Prevention of symptoms in cattle has been achieved by the use of licks containing 2 per cent of copper sulphate, by putting copper sulphate in drinking water or by spraying copper sulphate on

hay, the object of these methods being to supply each cattle

beast with about 3.5 g. per week throughout the year.

The most effective, simple and cheap means of controlling the disease in both cattle and sheep is to topdress the pastures with copper sulphate, using 5 pounds on each acre each year in the autumn topdressing (31). The copper sulphate can be employed alone or mixed with lime or any of the usual agricultural fertilizers, the most common form being a commercially produced copperized superphosphate containing 56 pounds bluestone per ton. As a contribution to the problems of distribution of copper sulphate on difficult terrain it has been shown that spreading from aircraft is feasible (32).

With the widespread use of copper as a topdressing on copper deficient land, the problems in stock management have been solved; the diseases caused by copper deficiency have been banished and production has risen to normal.

Indiscriminate use of copper can, however, bring further problems, especially if sheep are exposed to excessive copper intake. This species is much more susceptible to copper poisoning than cattle (33) and in a few instances losses have occurred when the owner supplied too much extra copper where no deficiency existed. Topdressing with small amounts such as 5 pounds copper sulphate per acre, even on land not deficient in copper, does not raise the copper content of the pasture to dangerous levels; the greatest danger is in supplying copper containing licks to sheep.

## Copper and Soils.

The total copper content in soil is an imperfect measure of the copper that is available to plants and therefore offers very limited help in applying the results of soil classification to the mapping of areas that may prove deficient for grazing stock. Pasture copper is clearly the most informative measurement when the health of stock is the main consideration but pasture is not always available for all will be set.

is not always available for all soil types.

Wright and Johnston (34) have initiated work that may prove of considerable value in understanding the influence of parent material and history in the development of a deficiency of copper in various soils. The "available" soil copper is determined by the Aspergillus niger technique of Mulder (35) and a check on the interpretation of this determination is being made by comparing the results so obtained with the copper contents of pastures grown on the same soils.

A number of genetically different soil types (36) have already been examined. Whole suites of soils derived from certain parent materials, such as consolidated dune sands and some claystones, are deficient in available copper, and soils in these suites are regarded as having an INHERITED copper deficiency. For such soils there is commonly a very good correlation between the

"available" soil copper and the copper content of the pasture

grown on the soil.

In other soil suites low figures for "available" copper are found as the degree of leaching increases. The weakly leached members of a suite, usually clays or clay loams, give a relatively high figure for "available" copper, whereas the more strongly leached types in the same suite, commonly silt loams or sandy loams, have a much lower "available" copper. This is regarded as an ACQUIRED copper deficiency. In these cases the correlation between "available" soil copper and copper content of pasture is not as close as for inherited deficiency, although the correlation is better for soil types that lie remote from the threshold position.

Examples of results are as follows:

Inherited copper deficiency.

Example. PINAKI SUITE (Intrazonal, strongly weathered yellow brown sands derived from consolidated coastal sands).

	"available"		p.p.m. copper in pasture.
	in s	011.	
Weakly leached. Whananaki sand (0-4").	٠	1.6	4.1
Moderately leached. Red Hill sand (0.5")	) .	0.8	2.8
Very strongly leached.			
Te Kopura sand (0-5").		0.3	2.1

Acquired copper deficiency.

Example. MARUA SUITE. (Zonal, strongly weathered yellow brown earths derived from greywacke sand-stone).

800110):		
	p.p.m. copper "available" in soil.	p.p.m. copper in pasture.
Moderately leached. Marua		
clay loam (0-5").	5.9	6.5
Moderately to strongly leached.		
Waikare silty clay (0-4").	1.3	
Very strongly leached.		
Wharekohe heavy silt loam (0	-4''). 0.6	4.5

Organic soils are regarded as belonging to suites with an inherited copper deficiency as they have a very low total copper content and pastures are low in copper. The aspergillus niger technique invariably gives high figures and the cause of this anomaly is not yet explained.

The classification of soils into inherited and acquired copper deficiency types is important in forecasting the effect that agricultural practice may have on the copper status of the soil and in accurate mapping of present or potential copper deficient

areas.

#### Future Problems.

A problem for the future is the possible further increase in molybdenum content of soil and pasture on complicated copper deficiency areas. Some of the affected peaty soils lie on top of considerable depths of peat, the organic fraction of which can be expected to disappear in the course of time by slow oxidation leaving a new topsoil with higher mineral concentration. The pasture may then take up sufficient molybdenum to produce molybdenosis in grazing stock even when normal amounts of copper are present in the diet, and the difficulties which exist on the teart lands of Somerset (30) may appear here. Further knowledge of copper and molybdenum relations in animal metabolism must be acquired and a study of methods to promote leaching of molybdenum must be made so that feasible control methods can be devised for a farming system that depends almost entirely on pasture as fodder for the cattle.

Another problem concerns the leached sandy soils in which the soil and pasture has been shown to be very low in both copper and molvbdenum. The first difficulty might well be the failure of such soils to supply the molybdenum requirements of nitrogen fixing bacteria and therefore the failure to provide an adequate source of nitrogen for grass growth. If molybdenum fertilizers are used complicated copper deficiency might well develop in cattle. Clearly topdressing with copper and molybdenum mixtures is the answer, but data on appropriate levels to use on readily leachable soils has yet to be obtained. There is also need for information on the effect on stock health of grazing on pastures of low copper and low molybdenum content. The results of copper deficiency are known, but the possible effects of low molybdenum in addition have not been investigated. Because of the interrelationships already demonstrated between copper and molybdenum it may not be too much to postulate that some of the biological functions of copper depend upon the participation of molybdenum.

The relation of copper deficiency to fragility of bones in cattle and sheep is another problem which has yet to be examined fully.

## Enzootic Icterus.

This disease, known in Australia as chronic copper poisoning (37) and in South Africa as enzootic icterus (38), occurs in some parts of New Zealand. In the central part of the North Island it has been known for some years and most outbreaks occurred on one soil type—Mairoa ash. Recently a series of outbreaks have occurred in the Hawke's Bay district on another soil type—Takapau silt loam.

The disease, which affects only sheep, has associated with it some abnormality of copper metabolism, for one important fea-

ture is that the liver of affected animals contains high levels of copper, and symptoms of the final stages of the disease are in general similar to those of poisoning by repeated doses of copper. There is, however, no more than the usual amount of copper in the soil or in the pasture. Occurrence in New Zealand has been of a somewhat sporadic nature as the disease seldom occurs for more than a few years on any one area. This circumstance has, in fact, imposed a serious limitation to the study of the disease.

In connection with enzootic icterus there is a real need to know more about the copper metabolism of the sheep. This species has a number of unusual features in its copper metabolism: it differs from all other species in having higher amounts of copper in the adult liver than in the lamb liver, which probably means a greater tendency to store copper; it is much more susceptible than the bovine to chronic or acute copper poisoning; and sheep grazing on pasture display a considerable seasonal variation in copper content of the liver. These features all indicate some difficulty in handling dietary copper and thus may have some bearing on the end result in enzootic icterus.

Dietary molybdenum has the same effect on sheep as on bovines in reducing copper levels in the liver but the significance of this in relation to enzootic icterus is not by any means clear. Other related elements like tungsten and rhenium do not show

the same effect.

#### IODINE DEFICIENCY.

In parts of New Zealand both humans and domestic stock are subject to simple goitre. This is rather unaccountable since the disease is at present regarded as due at least in part to lack of iodine in the diet and since New Zealand is a long narrow country regularly subjected to the influence of winds carrying moisture and solids from the broad areas of surrounding sea. That solids from the sea are in fact returned to the land has been shown by Gibbs (39) who found that as much as 350 lb. per acre of salt is deposited in a year by rain at places within a few miles of the sea and 112 lb. per acre is so deposited at a point 30 miles inland. It is not unreasonable to suppose that an appreciable quantity of iodine would also be derived from the same source.

The first account of goitre in domestic stock in New Zealand was written by Gilruth in 1901 (40). Calves and lambs were reported to be suffering from enlarged thyroid glands and the occurrence of the disease was the more remarkable since the farm on which it occurred had been occupied for 16 years without any previous record of similar trouble. Such a report might well be written at the present day as sometimes even now a heavy incidence of goitre in young stock is found, frequently for the first time, on land that has been farmed in much the same manner for as long as 50 years. However, the failure of farmers

to report goitre may not indicate faithfully the absence of minor lesions, since cases have been seen of moderate enlargement of the thyroid gland in sheep which had all the outward appearances of excellent health.

Cattle, sheep and horses have been affected by iodine deficiency in New Zealand. The young may be born dead, hairless and with enlarged thyroids, or may die within a few days. In some flocks of sheep up to 50 per cent. of lambs have been lost from this cause.

Treatment of affected animals with iodine has in general proved successful. For example, young goitrous lambs which survive the first 3 days can usually be reared if dosed with solutions of iodine or potassium iodide; and regression of thyroid size in adults and prevention of further cases in young has been

claimed as a result of supply of iodized licks.

The disease has usually occurred on river flats or alluvial soils but no thorough examination of affected soil types has yet been made. This is now in the process of being done at Wallaceville by detailed mapping of all areas of known iodine deficiency amongst animals for later comparison with soil maps. A chemical survey conducted between 1930 and 1938 showed that enlarged thyroids of low iodine content in lambs sent to Meat Works originated from parts of Wellington, Nelson, Marlborough, Westland, Canterbury and Otago Provinces (41).

In respect to etiology it is generally agreed that low dietary iodine is at least one important cause. In New Zealand Hopkirk, Dayus, Simpson and Grimmett (42) found low soil and pasture iodine associated with one outbreak in lambs; Hercus, Benson and Carter (43) make the same claim concerning the human disease, and much overseas work is in the same strain. Nevertheless the irregularity of occurrence from year to year on the same land suggests that low soil and pasture iodine may not be the only cause of simple goitre. Shore and Andrew (44) and Orr (45) have shown that in human endemic goitre the dietary iodine is not always low. The possibility of positive goitrogenic factors such as have been found, for example in cabbage (46) and in brassic seeds (47), (48), should be more thoroughly investigated in connection with endemic goitre in animals. This investigation must start from the field and take into account such features as soil type, pastures and crops and their management as well as variation in environmental factors such as climate.

Until a more thorough understanding of etiology suggests some other treatment the method of control will remain the provision of additional dietary iodine; for this purpose the most convenient form is in mineral licks. Accurate assessment of the efficacy of this procedure is beset by many difficulties. Some goitrous sheep refuse iodized licks in spite of the use of suitable lures; the disease may not recur in successive years on the same property; and the stability of potassium iodide which is the salt

usually employed, is low when it is exposed in licks so that stock may not get iodine even if they eat the lick. No control can be exercised over the first two variables, but it is very necessary to discover some form of iodine that can be employed in licks and which will contain iodine readily available to the animal, yet be resistant to oxidation, leaching and other effects of exposure. Still further it is essential that this iodine containing compound be inexpensive. Some work has already been done in this field and attempts have been made to protect KI in licks by coating with calcium stearate (49), by including thiosulphate, or by making licks slightly alkaline. Simple iodinated proteins not active as thyroproteins or other stable organic compounds of iodine might also be suitable.

The use of licks is always a hazardous method of supplying minerals to stock and application of the missing element to the pasture as a topdressing is preferable. This has not yet proved practicable with iodine on account of cost and because many factors such as soil pH and pasture species (50) modify the uptake of iodine by plants. A solution to these problems would be of extreme value. One possible line of experiment is topdressing trials with some of the newer resin exchange materials with iodine absorbed on to them. Such materials may give up iodine slowly over a long period and thus prove suitable and economic

for topdressing.

## OTHER ELEMENTS

The trace element deficiencies already dealt with are the only ones of direct importance to the health of animals. Others, most of which affect plants only will be mentioned very briefly.

Fluorine.

The fluorine content of most river waters in the North (51) and the South Islands (52) is less than 0.5 parts per million and is, therefore, below the level that is commonly regarded as necessary in drinking water to provide for optimal formation of tooth enamel. This deficiency may have some effect in rendering the human population susceptible to dental caries. There has been no direct association of dental abnormalities in animals with the low fluorine of water.

Molybdenum.

A soil deficiency of molybdenum has been found to be the cause of whiptail in cauliflowers (53) and this disease can be prevented by the application of ammonium molybdate as a fertilizer to the soil (54). The increased growth of pasture that results from molybdenum topdressing in certain localities has also been taken as an indication that a deficiency exists.

Chemical determination of the total molybdenum content of soil is not a satisfactory measure of molybdenum status because of the great difference of availability of this element in different soils and under different conditions of pH. Davies (55) has examined a number of laboratory methods for measuring availability and has reached the tentative conclusion that Tamm's oxalate extractant gives the most reliable measure. Observations on Okaihau gravelly silt loam illustrate the importance of availability. This soil contains over 9 parts per million total molybdenum and 0.07 p.p.m. soluble in oxalate solution. The low availability thus indicated is confirmed by an increased growth of pasture, which results from topdressing with molybdate. Other soils with much less total molybdenum but with a higher oxalate soluble fraction show no response to molybdenum fertilizers. Availability of molybdenum is increased by liming and it is not unlikely in some cases that apparent response to lime may be due in fact to increase of available molybdenum.

## Manganese.

No deficiency of manganese has been observed. On the contrary there have been observations which point to some soils having an excess of active manganese that retards plant growth. The application of sufficient lime reduces the available manganese to a level that is tolerated by plants. An example of this phenomenon is Davies' (55) work on Ngaio silt loam. In pot experiments he found that the untreated soil supported only very limited growth of subterranean clover. The herbage that did grow contained a very high concentration of manganese. Limed pots grew much more clover with a very much smaller content of manganese.

#### Boron.

Boron deficiency causes brown heart of swedes (56) and internal cork of apples (57). These diseases are of considerable importance in New Zealand and are controlled by application of boron as a fertilizer. Some soils are naturally deficient in boron; in others, especially those on the threshold of boron sufficiency, the deficiency may be induced by heavy applications of agricultural lime.

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## BANQUET AND BUSINESS MEETING

The Tenth Annual Banquet was held at the Haven Hotel on the evening of June 22, 1950. This was a particularly auspicious occasion because of the impending election of ten Honorary Life Members to the Society of a world wide selection in view of their contributions to Soil Science and to Agriculture. The election of an additional member from the field of medicine to be known as our "Country Doctor" was of particular interest and not intended to merely signify our recognition of the growing importance of the relationship between soil science and health, of man and beast alike, but also to call the attention of the State and of the Nation to one of Florida's oldest and most faithful practitioners who, himself, has been conscious of this important relationship for many, many years. In fact he always sought to enlarge his knowledge in this field through the years and to use it as a veritable cornerstone for his medical practice.

The Guest Speaker for the occasion was Dr. Edward Mac-Arthur Redding, Director of Research, Charles F. Kettering Foundation, Dayton, Ohio. His subject was "Photosynthesis—A Link Between the Sun and the Soil." Dr. Redding's lecture as well as the introduction of the Honorary Members, will be found at the front of this volume. The presentation of these nominations was made by the Secretary with the exception of Dr. Charles F. Kettering who was introduced by Dr. Redding and Dr. John G. DuPuis, M.D. whose life work was very ably reviewed by Mr.

Nixon Smiley of the Miami Herald.

#### BUSINESS MEETING

The Business meeting was of necessity very short and consisted of little more than the report of the Nominating Committee, Dr. E. L. Spencer, Chairman and of the Resolutions Committee, Mr. Luther Jones, Chairman. The former in reporting on the action of his committee, which included Mr. F. E. Boyd and Mr. J. R. Henderson, nominated Dr. I. L. Wander for Vice-President, this being the only elective position open each year. In the absence of any nominations from the floor upon call from the Chairman, the usual motion was made by Dr. G. M. Volk and seconded by Mr. R. N. Edwards, and carried, that the Secretary be instructed to cast a unanimous ballot for the nominee. The report of the Resolutions Committee is to be found on the following page.

The report of the Secretary-Treasurer and of the Editor were oral and brief. In the matter of dedication of Proceedings Volume X it was decided that this should be to the ten Honorary Life Members who were formally received into the Society during the evening and who, along with Dr. DuPuis, have so graciously

accepted this recognition which the Society has extended.

### MEETING OF THE EXECUTIVE COMMITTEE

The only matters taken up at a brief meeting of the Executive Committee were the appointment of a Secretary-Treasurer, R. V. Allison, Belle Glade, and a discussion of the feasibility of including a well-developed symposium on fiber crops in South Florida for inclusion in the program of the next annual meeting to be held in West Palm Beach. The plan was generally approved and the further thought extended that it would be a good idea to include a field trip on this same subject if satisfactory arrangements could be made to that end.

## RESOLUTION OF SYMPATHY

## Soil Science Society of Florida

Whereas, death has taken from our rolls during the year 1950 the following esteemed members of the Society whose sincere and constructive interest in all aspects of the work will make their absence keenly felt for a long time to come,

Now Therefore, Be It Resolved, that this expression of sorrow over this great loss and of sympathy to the immediate families of the deceased be spread upon the records of this Society and a copy of same be sent to the closest member of the family of each.

Dr. Oskar Baudisch Saratoga Springs, N.Y.

Mr. Daniel W. Beardsley, Sr. Clewiston, Fla.

Dr. M. A. Brannon Gainesville, Fla. Mr. R. O. Couch Melbourne, Fla.

Mr. G. Milton Fisher Westboro, Mass.

Mr. Charles T. Fuchs South Miami, Fla.

By the Resolutions Committee, Luther Jones, Chairman.



DR. W. T. FORSEE, JR.

# RETIRING OFFICERS OF THE SOCIETY (1950)

W. T. Forsee, Jr.	President
RICHARD A. CARRIGAN	Vice President
HORACE A. BESTOR	Mbr. Exec. Committee
R. V. ALLISON	Secretary-Treasurer

#### APPENDIX

# The Minor or Trace Elements in Soils, Plants and Animals\*

### W. O. Robinson\*\*

This leaflet has been prepared as a reply to numerous requests for information as to what chemical elements are needed for normal, healthy plant and animal development, how to restore "trace minerals" to the soil, and similar inquiries.

The whole subject is now in a state of flux due largely to the lack of accurate, fundamental knowledge of the quantities present and essentiality of the various minor elements in soils, plants, and animals. The availability of these elements to the plant varies a great deal with the chemical and mineral combinations and soil conditions in which they occur. The problem is still further complicated by our lack of knowledge of the complex organic compounds such as enzymes, vitamins, and biotics, in which these elements function in the chemical metabolism of the plant.

The minor or trace elements have acquired the following meaning: They are present in very small quantities in the plant and animal, generally less than 500 parts per million on the dry weight basis. They are generally, but not necessarily, essential to the plant or animal, though in some cases they may be poisonous to those organisms. The minor elements are commonly removed from the soil by plants in greater quantities than many soils can supply for considerable periods of time, or are required by the animal in quantities greater than supplied by the plant grown under some soil conditions.

The more important minor elements are iron, boron, manganese, copper, zinc, cobalt, iodine, selenium, and molybdenum. Some of these are not necessary for plants but are required by animals. Iodine and cobalt are such elements. Molybdenum appears to be necessary in very small quantities for plants but not necessary for animals, in fact it is toxic to ruminants if present in forage in quantities exceeding 6-10 parts per million. Both molybdenum and selenium are taken up in considerable quantities by plants and have very little effect on the plants, though the selenium in the plant is toxic or even lethal to animals.

There is nothing mysterious about the essentiality of the chemical elements to plants and animals. It is the natural out-

<sup>\*—</sup>A mimeographed release prepared shortly before the Winter Haven meetings.

<sup>\*\*—</sup>Senior Chemist, Soils Division, Bureau of Plant Industry, Soils and Agricultural Engineering, U. S. Department of Agriculture, Beltsville, Md.

growth of the evolution of the plant and animal forms we now have. They can be considered as very delicately adjusted laboratories having to make use of the elements in their environment. The order of abundance of the elements seems to be one requirement of essentiality but the essential element also has to perform some useful chemical reaction.

Through the geologic ages during which evolution has taken place, the organisms which could best adapt their chemistry to make use of the raw materials, in this case the chemical elements, and the source of energy, the sun, have survived. The question as to whether an element is essential or not depends upon whether this element has been useful to the organism in surviving through the ages. Changes have taken place in plant and animal environment, temperature changes, and changes in the composition of the atmosphere.

The bodies of plants and animals are largely composed of water. The chemistry of metabolism is a water chemistry in which varying degrees of solubility are most important. It is supposed that animal life developed in the sea where the organism had a great variety of elements at its disposal. Animal digestion is primarily an acid digestion dependent upon hydrochloric acid derived from sodium chloride, the most prominent salt in sea water.

At this point it is interesting to consider the abundance of the elements on the earth's surface. This has been calculated for a shell 10 miles deep including the atmosphere and the oceans—This order of abundance is:

(1) Oxygen 49.10 percent, (2) Silicon 26.00, (3) Aluminum 7.45, (4) Iron 4.20, (5) Calcium 3.25, (6) Sodium 2.40, (7) Magnesium 2.35, (8) Potassium 2.35, (9) Hydrogen 1.00, (10) Titanium 0.61, (11) Carbon 0.35, (12) Chlorine 0.20, (13) Phosphorus 0.12, (14) Sulfur 0.10, (15) Manganese 0.10, (16) Fluorine 0.08, (17) Barium 0.05, (18) Nitrogen 0.04, (19) Strontium 0.035, (20) Chromium 0.03, (21) Zirconium 0.025, (22) Vanadium 0.02, (23) Nickel 0.02, (24) Zinc 0.02, (25) Boron 0.01, (26) Copper 0.01, . . . (32) Cobalt 0.002, . . . (38) Molybdenum 0.001, . . . (56) Iodine 0.0001, . . . (62) Selenium 0.00008.

The order of abundance of the elements in plants and animals may be approximated:

(1) Oxygen, (2) Carbon, (3) Hydrogen, (4) Nitrogen, (5) Calcium, (6) Potassium, (7) Magnesium, (8) Phosphorus, (9) Sulfur, (10) Iron, (11) Manganese, (12) Boron, (13) Zinc, (14) Copper, (15) Chlorine, (16) Sodium, (17) Fluorine, (18) Iodine, (19) Cobalt.

The most abundant elements in plants are the atmospheric elements from which organic matter is largely metabolized. They

make up sugars, starches, cellulose, fats, etc., and the bulk of proteins and more complex organic substances. The atmosphere is the main environment of most plants and animals, and water organisms depend upon dissolved oxygen for energy.

To carry on the side chemical reactions that take place through photosynthesis to metabolism, the plant has made use of the most abundant elements at its disposal that would perform the necessary chemical reactions. In the average soil solution and river water, calcium is the most abundant alkaline element and next to the main atmospheric elements it is the most abundant element in plants. Part of the function of calcium is to remove a side product of photosynthesis, oxalic acid, which it does by precipitating the insoluble calcium oxalate.

The more abundant elements that are not useful to plants and animals are the very insoluble elements in the combinations in which they occur. Thus, of the first fifteen in order of abundance, only three, silicon, aluminum and titanium, are not essential to the majority of organisms, at least in anything more than traces.

More detailed descriptions of the minor elements in plants and animals follow:

#### Iron

Iron has long been recognized as essential for healthy plant development. It is directly connected with the functioning of the chlorophyll in plants and the red blood corpuscles in the animal. In the leaves of healthy plants iron will average a few hundreths of one percent (dry weight basis), the quantity never

varying greatly.

Although there is an abundance of iron in nearly all soils, the soluble or exchangeable iron in calcereous or other soils around the neutral point may be so low that plants are unable to absorb enough for healthy growth. The solubility of iron in the soil is governed by the reaction of the soil, the element being comparatively soluble in very acid soils and also by the prevalence of reducing conditions. The submerged soil conditions that occur in very wet weather are favorable for the solution and transportation of iron in the soil solution and in extreme cases the concentration of iron may exceed the toxic limit.

The addition of any reducing organic matter such as crop residues, stable manure, or compost increases the supply of available iron in the soil. The iron is temporarily reduced and made soluble and the complex ions formed with the organic matter hold the iron, even after oxidization, in solution at pH concentrations that would otherwise precipitate the insoluble ferric hydroxide. Plants are sometimes sprayed with solutions of ferrous sulphate to cure iron deficiency. In Hawaii, the pineapple crop is sometimes sprayed four times a year with an 8 percent

solution of ferrous sulphate.

#### Boron

Boron, from the standpoint of agriculture, is unique among the chemical elements in that very small quantities are necessary for the growth of many, if not all plants, and only slightly higher concentrations cause injury. With a number of plants the range between these two levels is only a few parts per million.

Boron is present in quantities up to 200 parts per million in all normal, healthy plants. Orchard-grown citrus leaves suffering from boron injury may contain in excess of 5 times as much. Soils contain from 3 to 90 parts per million total boron. Only a small portion of this boron is water soluble. In New Jersey one half part per million of water soluble boron in the soil is considered ample.

Many crops show boron deficiencies. The heart and dry rot of sugar beets, internal cork of apples, browning and hollow stem of cauliflower, yellows of alfalfa, cracked stem of celery, top rot of tobacco and brown or watery heart of turnips are

boron deficiency diseases.

Alfalfa yellows and failure of alfalfa to seed can be remedied by applying 20 to 60 pounds of borax to the acre. For tobacco no more than 10 pounds per acre should be used. For boron deficiencies in other crops varying quantities are used depending on the texture and composition of the soil. Special fertilizers for alfalfa contain 60 pounds of borax to the ton; this not only remedies alfalfa yellows but greatly increases the yield of seeds.

The availability of boron is much less in calcareous than in acid soils. In some calcareous soils the soil application of borax is not effective. It is necessary to spray the plants. Three pounds

of borax in 100 gallons of water make a suitable spray.

As before mentioned boron is quite toxic and much injury has resulted in the past from using potash salts which contained boron in harmful amounts. Borax even at the rate of 30 pounds per acre may cause injury to sensitive crops in very dry seasons on sandy soils.

# Manganese

Manganese is a common constituent of soils and plants, the quantities present in both varying greatly. In many soils and plants manganese is a major element. Certain Hawaiian soils contain as much as 15 percent Manganous oxide, and some soils in the United States contain over 3 percent. Some plant leaves, particularly the forage legumes contain as little as a few thousandths of one percent, and a number of tree leaves growing on very acid soil contain over 0.5 percent.

Some soils contain only a very small quantity of manganese. Others containing much manganese may have it in an unavailable form such as the very insoluble dioxide. This latter condition obtains in calcareous and other alkaline soils, and in any

soil immediately after heavy liming. There is no correlation between the total manganese in soils and in plants growing on these soils. The availability is governed rather by the acidity and reducing action of the soil than by the quantity present. The exchangeable manganese in forest leafmold commonly equals and sometimes exceeds the exchangeable calcium.

The manganese in soils containing organic matter becomes very soluble when these soils are submerged for relatively short periods. Under these conditions the concentration of soluble manganese exceeds the limits that have been found to be tolerated by plants. On acid soils, injury to tobacco, pineapples, beans and other crops by excessive quantities of manganese has been noted.

There are a number of deficiency diseases due to lack of available manganese in the soil. These are chlorosis of tomatoes and other plants on highly calcareous soils. The "marsh spot" of peas and "gray speck" of oats occurs on organic soils in the British Isles and Northeastern Europe.

Manganese deficiency has been noticed in animals. It causes "slip tendon" or perosis in chickens, also low hatchability of eggs. Low manganese in feeds also causes lameness in pigs and sterility in bovines.

The quantity of manganese that must be supplied on soils to correct the shortage may vary, but additions of 25 to 50 pounds of manganous sulphate per acre have resulted in remarkable increases in crop yield on certain soils.

## Copper

Copper is 26th in order of abundance in the earth's crust, the average being 100 parts per million. Soils average considerably lower than this. Leaves of green plants seldom contain less than 5 p.p.m. or more than 20 p.p.m. Copper is said to be concentrated in the seeds of plants. In the corn seed, the germ contains 20 p.p.m. and the endosperm 0.5 p.p.m.

Copper deficiency in vegetables is confined to those grown on high organic soils. In some of the rich organic soils in the Everglades of Florida lettuce, celery, and other vegetables cannot be grown without the addition of from 25 to 50 pounds of copper sulphate per acre. A disease of citrus, pears, prunes, and other fruits, exanthama or die back, and also the reclamation disease are caused by a deficiency of copper.

In the animal, copper is necessary for the utilization of iron in the formation of haemoglobin. Piglet anemia and sway back of lambs are due to copper deficiency. "Stringy" wool of sheep (Australia), "Scouring disease" (Holland), "Licking disease" of ruminants (Europe), "Coast disease" of grazing animals (Australia) and "Salt sick" of cattle (Florida) are due to a dual deficiency of copper and cobalt.

Zinc is the 24th element in order of abundance in the earth's crust. It is present there at the average of 200 p.p.m. Soils vary a great deal in zinc content ranging from a little less than 5 p.p.m. to over 200 in soils of considerable extent. The range in plants is much greater; from 5 to over 5000 p.p.m. It is odd that the plant can accumulate so much zinc without showing any toxic effect.

Plants suffer a number of deficiency diseases due to lack of available zinc. They are "Little Leaf," or "Rosette" of apples, pecans, vines, and stone fruit; "Mottle Leaf" of citrus, "Yellows" of walnut, "Bronzing" of tung trees, and "White Bud" of corn. Animals appear to get an abundance of zinc in the plants they consume.

Zinc forms about 0.3 percent of carbonic anhydrase, a respira-

tory enzyme found in both animals and plants.

Zinc sulphate is applied as a spray or directly to the soil to correct deficiency diseases. Up to 25 or even 50 pounds per acre have been used and in certain calcareous soils as much as 200 pounds per large pecan tree have given economic increase in crop yields.

#### Cobalt

Cobalt is of interest because it is necessary especially for cattle and sheep. Only about a milligram per day is necessary even for a large animal. For over two centuries it has been known that certain pastures in the British Isles produced "pining" in cattle and sheep. Long ago this disease was correctly ascribed to the forage but not until nearly 20 years ago was the real cause known. It is a cobalt deficiency disease. Cobalt deficiencies are found in a number of places in the United States.

Cobalt does not appear to be essential to plants. However, it is necessary for cattle foods to contain as much as 0.08 p.p.m. for complete animal health. Cobalt is given as a mineral supplement or drench. In New Zealand it is used at the rate of two pounds of cobalt sulphate per acre applied with super-

phosphate.

### Iodine

Iodine deficiency is the classical animal deficiency disease. And unlike the rest of the minor elements, the deficiency was first found in humans. Later it has been traced to various domestic animals. Lack of sufficient iodine in plants and water causes goiter. Iodine does not appear essential to plants but is taken up by them in amounts ranging from 20 to 200 parts per billion. These are average quantities for various plants used as foods. Occasionally plants are lower and some very much higher.

The goiter belts are generally on coarse, gravelly, sandy soils having little clay or organic matter, or in areas profoundly leached by melting snow. In the earth's crust iodine is 56th in order of abundance, or one part per million. It is the least abundant element which has been definitely proven essential to animals.

Like salt, sodium chloride, it has been found practical to supply this element artificially. The need for salt was intuitively shown by the craving for salt before the dawn of history, but it took years of patient chemical research to connect goiter and

cretanism with iodine deficiency.

## Molybdenum

Molybdenum is of interest because minute quantities are required for nitrogen fixing bacteria, and in some places pasture plants take up enough of this element to be definitely toxic to

cattle and sheep.

In some places in Australia economic responses in yields of subterranean clover have been realized by the application of as little as one ounce of molybdenum per acre. Elsewhere molybdenum deficiencies in soils in the field have not been observed, though some soils have been found molybdenum deficient in greenhouse tests.

In the earth's crust molybdenum is 38th in order of abundance, the average being 10 p.p.m. In over 200 representative American soils molybdenum averages 2.6 p.p.m., 85% of these soils range between 1 and 4 p.p.m. In plants and plant parts the range is from less than 0.1 to over 400 p.p.m., though forage

plants seldom exceed 10 p.p.m.

In some parts of the British Isles and in some parts of California and Florida the vegetation has been found to exceed 10 p.p.m. molybdenum. Cattle fed on such pasturage become unthrifty and sometimes die. Molybdenosis in cattle is not only dependent upon the quantity of molybdenum in the plant but also upon the copper content, for these two elements appear to be antagonistic in the ruminant. Molybdenosis has been cured by feeding the animal 1 to 2 grams copper sulphate daily.

The quantities of molybdenum that plants will take up is greatly increased by making the soil alkaline with calcium carbonate. It is of low availability in acid soils. In "black alkali" soils molybdenum availability would be very high. This property of molybdenum, (also selenium), is quite the opposite from iron, manganese, zinc, cobalt and copper, the availabilities of

which are decreased by overliming.

Phosphate rock, from which superphosphate is made, generally contains molybdenum, and some Florida and Western phosphates contain as much as 50 to 200 p.p.m. Superphosphate makes up the bulk of mixed fertilizers, and it is believed that no soil deficiencies of molybdenum will occur on soils that are

fertilized with commercial fertilizer. On the other hand, no fears are anticipated that the use of superphosphate will cause molybdenum toxicity in cattle for superphosphate applications reduce rather than increase the molybdenum content of vegetation.

#### Selenium

This element is of interest because of its extremely poisonous properties. Enough of it is taken up by certain plants to be lethal to animals eating even small portions. Such poisonous plants appear perfectly healthy. They have adapted their chemistry to use selenium; it may even be essential to their development.

Selenium is even somewhat rarer than iodine. It is, however, concentrated under some conditions of soil development. When certain cretaceous shales form soil under semi-arid conditions, selenium becomes available to plants. All soils contain some selenium, but it is only under semi-arid conditions, in alkaline soils, in presence of calcium carbonates and sulphates that plants take up enough to be poisonous. Highly ferruginous soils of Hawaii, Puerto Rico, and Southern Texas may contain as much as 10 p.p.m. selenium and not produce toxic vegetation whereas soils formed from Pierre Shales in South Dakota, Wyoming and other nearby States may contain only 0.5 p.p.m. and produce lethal vegetation.

Sprays containing selenium are very effective in controlling red spider. Sodium selenate is used in low concentrations in greenhouse soils to kill aphids, red spiders, and foliar nematodes. Enough of the element is taken up by the plant to kill these insect pests. Food plants raised on soil so treated may be quite poisonous. Great care should be exercised in using selenium

sprays on plants and sodium selenate on the soil.

## Other Elements

Considerable fluorine is let loose into the atmosphere by industrial processes such as the manufacture of aluminum, superphosphate, bricks, glass, steel, high octane gas and some chemicals. This gas is quite toxic to vegetation, and to cattle and sheep feeding on fluorine contaminated vegetation. Fluorine is not taken up from normal soils by the plant in injurious quantities. Fluorine in quantities of about 1 p.p.m. in drinking water seems to exert a beneficial effect on human teeth.

Barium and strontium are present in more than traces in most plants. Barium may reach as high as 0.2 percent in some leaves. Those elements seem to have little or no effect on plant and animal growth in the quantities they occur in vegetation.

Barium carbonate is quite poisonous to animals.

The rare earths as a group appear to act as one element biochemically. They are present in the earth's crust as 0.018 percent

and the group would be 25th in order of abundance. They form relatively insoluble oxalates, and may function as calcium in plant growth. Hickory leaves may contain as high as 2000 p.p.m. rare earths. These elements appear to be present in small quantities in all plants. Rare earths presumably concentrate in the skeletal structures of animals. Very little is known about the physiological reaction of the rare earths on animals.

Sodium, chlorine, silicon and possibly aluminum form a group of elements, which although not absolutely essential, are definitely beneficial to some plants under some conditions. Silica

is especially high in the grasses.

Through further research it may develop that other elements may be essential to plant or animal life even when present in such very small, or smaller, quantities than iodine. Given an abundance of sample and a sensitive and exhaustive method of chemical analysis, it is believed that nearly all the elements, except perhaps the rare gases, could be shown to be present in plants and animals. Silver, lead, tin, gallium, germanium, and even gold have been found in many plants. It is not known whether their presence is merely accidental or if they serve some useful purpose.

The various State Experiment Stations are familiar with the minor element requirements of plants and animals. These requirements naturally vary with local conditions and the County Agricultural Agent and State Experiment Station should al-

ways be consulted.